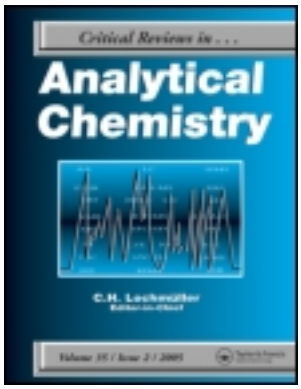

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Olive Oil Aroma Evaluation By Gas Chromatographic Method: A Critical Review

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The virgin olive oil aroma evaluation has been applied as a quality and authentication control technique. Many analytical procedures have been used to identify and quantify the volatile components that characterize olive oil flavor. Among of them, gas chromatography is the main technique applied for this purpose. This study carries out an extensive and complete review of all the works published, since 30 years ago to the present, that have used gas chromatography technology for olive oil aroma analysis. Special attention has been devoted to the olive oil volatile compounds extraction and concentration techniques and separation and identification methods applied.

Keywords gas chromatography (GC), olive oil, volatile compounds, aroma

INTRODUCTION

Aroma is an important criterion for virgin olive oils (VOO). Consequently, the identification of the compounds contributing to this aroma is considered a key for quality and authentication control. In fact, volatile components of olive oil are of a big interest since they are related to its quality and are used to detect adulteration (Cavalli et al., 2004).

Olive oils are complex mixtures consisting of two main groups of substances: (a) saponificable substances which represent nearly 98% of the chemical composition, such as tryglycerides, partial glycerides, and esters of fatty acids of free non-esterified fatty acids; and (b) unsaponificable substances, with many different chemical structures, which represents only 2% of all olive oil composition, such as sterols, hydrocarbons, pigments, phenols, flavonoids, or volatile compounds (Aparicio and Aparicio-Ruíz, 2000).

These volatile compounds are mainly responsible for the flavor of olive oil, which is of prime importance in the food industry because it plays a significant role in consumer choice. C_6 and C_5volatile components are mainly responsible for the "green" odor notes of olive oil aroma, and they are characteristics of the good quality of VOO required by consumers (Angerosa, 2002).

Many analytical procedures have been used to identify and quantify the volatile components that characterize olive oil aroma. Among of them, gas chromatography (GC) is the mainly used separation method because it can easily identify the components of a mixture and offers a high resolution for organic volatile compounds detection.

Since 30 years ago, many works have been published on the utilization of gas chromatographic technique for the analysis of vegetable oil volatile compounds. Some were oriented towards the study of off-flavor compounds in refined oil (Jelen et al., 2000), while others more specifically addressed to the study of aroma compounds in extra VOO (Servili et al., 1997; Contini et al., 2000; Vichi et al., 2003; Tura et al., 2004). The aim of this work has been the review of all the works published that have been used gas chromatographic technology in the olive oil field from 1980 to the present. Particular attention has been devoted to the olive oil volatile compounds extraction and concentration techniques and separation and identification methods applied.

ORIGIN OF THE GAS CHROMATOGRAPHIC METHOD

Chromatography dates to 1903 in the work of the Russian scientist, Mikahil Semenovich Tswett, who used a column filled with calcium carbonate powder to separate the pigments of green leaves. This author coined the word "chromatography" from the Greek words "chroma" and "graphein", which mean "color" and "writing," respectively. In 1947, German graduate student Fritz Prior developed solid state GC. But Archer John Porter Martin, who was awarded the Nobel Prize for his work in developing liquid-liquid (1941) and paper (1944) chromatography, laid the foundation for the development of GC and later produced liquid-GC (1950) (Poole, 2003).

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GAS CHROMATOGRAPHIC ANALYSIS

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. It uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time) (Bélanger et al., 1997).

ADVANTAGES AND DISADVANTAGES OF THE CHROMATOGRAPHIC METHOD

This mechanical method is not a time-consuming and automated system (Gardner and Bartlett, 1994). It is very good at separating complex mixtures into components. It is a fast analysis technique (typically minutes) and has high resolution and very high precision. It needs small amounts of sample with little preparation, but it presents excellent sensitivity to detect volatile organic mixtures at low concentrations. This equipment is not very complex and can be coupled to other techniques, e.g., mass spectrometry (MS) (García-González and Aparicio, 2002; Cornetto-Muñiz, 2003; Jiménez et al., 2004).

Although the analysis of the volatile compounds by chromatographic method is a powerful separative technique, most analyses require a little sample preparation, so that real-time analysis is difficult (Capone et al., 2003), i.e., it cannot be applied on-line in the olive oil storage and bottling process in an olive oil mill (García-González 2002; García-González 2004). The GC technique is not useful for an olive oil sensory evaluation because there is not a good relationship between volatile compound composition and sensory perceptions, since several chemical factors affect the odor intensity more than their concentration.

STATIONARY PHASES SELECTION

The successful development of the gas chromatographic method depends on the correct decision on the stationary phase used (Burns, 1986). Stationary phases employed in GC can be divided in two groups (Valcárcel and Gómez, 1990):

- Solid adsorbents, applied in adsorption gas chromatography (AGC) or gas solid chromatography (GSC).
- Liquid phases, coated onto a solid substrate and used in gas liquid chromatography (GLC).

Actually, the interest in GSC is due to the wide availability of porous covers of the capillary columns, such as porous-layer open-tubular (PLOT) columns, because they are more permeable and longer, they supply more defined beaks, and have major capacity of regeneration in comparison with packed columns (Poole, 2003). The principal adsorbents used in GSC are detailed in Table 1.

TABLE 1
Adsorbents Used in GSC

Adsorbent	Applications
Inorganic oxides (silica gel and alumina)	Hydrocarbons saturated and unsaturated with low molecular weight
Graphite charcoal, coated with Carbowax 20M	Volatile compounds, such as alcohols, aldehydes, ketones, terpens, hydrocarbons and industrial solvents
Graphite charcoal, coated with molecular sieves	Inorganic gases, hydrocarbons C1-C3 and small polar molecules
Molecular sieves	Permanent gases (oxygen, hydrogen, nitrogen and carbon monoxide)
Polymer porous (Tenax-GC)	Polar compounds with high boiling point

The use of a liquid compound as a stationary phase in GLC has two principal advantages: the quantity of liquid phase in a column can be easily modified and a high number of liquid stationary phases are available. But, the main disadvantage of liquid phases is their volatility. However, there are many liquid stationary phases that work at low pressure and high temperatures inside the column (Burns, 1986). The principal liquid stationary phases used in GLC are: Hydrocarbons and perfluorocarbons (PFCs) such as hexadecane, squalene, apolane-87, and Apiezon fats, which are mainly used as non-polar stationary phases; Organic liquid salts, which have favorable properties of mass transfer and low chemical reactivity; Ethers and esters, such as phthalates, and phenyl esters, which are useful to analyze liquids with low molecular weight due to their low volatility, or polyethylene glycol compounds, such as Carbowax 20M, which is the most popular polyethylene glycol compound used as stationary phase in wall-coated open-tubular (WCOT) columns because of their excellent coating characteristics (Poole, 2003); and Polysiloxanes, such as OV series, which are the most popular liquid stationary phases used in GLC due to their properties—they work in a wide range of temperatures, they have good solubility to different solutes, and excellent capacity films formation.

SAMPLE INTRODUCTION SYSTEM

Solid, liquid, or gas samples can be analyzed by gas chromatography (Valcárcel and Gómez, 1990): Liquid samples are the most commonly used and two systems are employed, rotator valves and injection syringes; Gas samples are mainly introduced in the gas chromatograph using rotator valves; Solid samples are dissolved and they are introduced as a liquid sample; and Headspace chromatography, which is employed to determine the volatile compounds of solid or liquid samples placed

inside a hermetically sealed container, by analysing of the vapor phase that is in equilibrium with the sample. There are two methods to analyze the headspace of a sample: static headspace (SHS) and dynamic headspace (DHS), which will both be described later.

COLUMN SELECTION

The column is the essential element in the gas chromatograph equipment because the components of a mixture are separated inside due to different chemical-physical processes based on adsorption or partition phenomenon. Two types of columns are used in GC:

- Packed columns are 1.5–10 meters in length and have an internal diameter of 2–4 mm. The tubing is usually made of stainless steel or glass and contains a packing of finely divided, inert, solid support material (e.g., diatomaceous earth) that is coated with a liquid or solid stationary phase. The nature of the coating material determines what type of materials will be most strongly adsorbed. Therefore, numerous columns are available that are designed to separate specific types of compounds.
- Capillary columns have a very small internal diameter, on the order of a few tenths of millimeters, and lengths between 25–60 meters are common. The inner column walls are coated with the active materials (WCOT columns) or some columns are quasi-solid filled with many parallel micropores (PLOT columns). Most capillary columns are made of fused-silica with a polyimide outer coating. These columns are flexible, so a very long column can be wound into a small coil.

The main difference of these types of columns is its permeability; therefore, capillary columns put up low resistance to the mobile phase flow and can be longer than packed columns (Poole, 2003).

DETECTION SYSTEMS OF THE SAMPLE

A gas chromatograph has a continuous detection system to indicate and quantify the separated solutes that come from the column. The main detectors used in GC can be classified in four groups according to the physical method of detection employed (Poole, 2003):

a) Thermal conductivity detector (TCD), mainly used for permanent gases, hydrocarbons with low molecular weight, and compounds not detectable with FID.
b) Ionization detector:
   b.1) Flame ionization detector (FID) is the most popular detection system. It presents low detection limits, simplicity in operation, stability, quick answers, and wide linearity range.
   b.2) Thermoionic dectector (TID) is very used to detect pesticides because of it is very selective and sensitive to compounds with nitrogen, phosphorous, and alkaline metals.
   b.3) Electron-capture detector (ECD) is widely employed in environmental analyses due to its high specificity and non-destructive system.
   b.4) Photoionization detector (PID) is used in environmental applications, too, such as aromatic hydrocarbons or vinyl chloride.
   b.5) Helium ionization detector (HID) is universal and extremely sensible and it is utilized to analyze permanent gases and volatile compounds that are at concentrations to be detected too low by TCD or FID.
c) Electrolitic conductivity detector (ELCD)
d) Spectroscopic detector:
   d.1) Flame photometric detector (FPD) is employed with compounds with heteroatoms, such as S or P.
   d.2) Chemiluminescente detector (CD) — their principal applications are based on the determination of nitroamines and volatile compounds with sulphur.
   d.3) Atomic emission detector (AED) can be used to detect unstable compounds with stable isotopes.

OLIVE OIL VOLATILE COMPOUNDS EXTRACTION TECHNIQUES

The composition of the headspace of a virgin olive oil is highly complex. It is composed of over 100 components, most of which are present at very low concentrations, just a few ppm or even less (Contini and Esti, 2006). For this reason, an extraction-concentration of volatiles prior to GC analysis is required, usually carried out using headspace sampling techniques (Angerosa et al., 1997; Morales et al., 1994). This process can be developed by different methods (Morales and Tsimidou, 2003):

Techniques Without Concentration

a) Direct injection is the simplest technique and it doesn't need manipulation. However, it is less sensible due to the fact that it manipulates low a quantity of sample and it needs a high work temperature and a perfect cleaning process of the chromatographic column after each sample to avoid contamination and "memory effect" (Morales and Tsimidou, 2003). This technique has been widely applied in vegetable oils (Warner and Frankel, 1985).
b) SHS a solid or liquid sample is put inside a hermetically sealed container. This container is heated until there is equilibrium between the sample and the vapor phase, called headspace. A syringe with an adsorbent fiber adsorbs part of this gas phase and this syringe is introduced into the gas chromatograph where the desorption of the volatile compounds take place. SHS is a quick and simple technique because it doesn't need sample preparation or solvent use and it presents high repeatability and good linearity.

However, this technique needs large sample volumes and it isn't useful to concentrate volatile compounds with low molecular weights (Cavalli et al., 2003). This method has been extensively utilized for olive oil applications.

Techniques with Volatile Compounds Concentration

a) Distillation is the technique most applied to isolate volatile compounds of foodstuffs. Vacuum distillation and distillation with vapor flow are the methods most applied.
b) Distillation – simultaneous extraction — the sample dissolved in water and the solvent distil separately and condense on the same zone where the extraction takes place. The advantages of this method are that a small quantity of solvent is used, obtaining a high concentration of volatile compounds in a short time and reduction of the thermal degradation because it works with a reduced pressure. However, this method is not useful to concentrate thermo-labile compounds. This technique has not been frequently used with vegetable oils (Morales and Tsimidou, 2003).
c) DHS / Purge and trap (P/T) — they are similar to SHS, but there is a continuous flow of gas over the sample which carries away the volatile compounds of the sample. In the case of DHS, the volatile compounds are swept from the surface of the sample with an inert gas. In P/T, an inert gas is burbled through the sample. Both DHS and P/T can use two types of traps: adsorbent and cryogenic traps. The first one consists & a vidrio tube filled with an adsorbent, such as activated charcoal, Tenax series, Porapak series, Chromosorb series, and Amberlite series, where the volatile compounds are retained. A cryogenic trap consists of a tube refrigerated with liquid nitrogen. The volatile compounds flow through the trap and condense inside. The volatile compounds adsorbed in both types of traps can be desorbed with solvents or thermal desorption.

   Desorption with solvents was frequently applied to olive oils in the 1980s and the DHS-thermal desorption was a very popular technique proven for its performance and widely used in a great number of studies for the isolation of the olive oil flavor compounds. However, not as much information has been available on the optimization of this technique in terms of purging time and temperature conditions.
d) Extraction with super critical fluids (SFE) is an alternative to traditional extraction techniques due to its advantages such as quick extraction times, high efficiency, and the ability to be coupled to other analysis methods, such as GC. However, the main disadvantage of SFE is the possible fugues that can get out a part of the volatile compounds responsible for the aroma of the foodstuffs. This technique has been applied to VOO volatile compounds.
e) Solid phase microextraction (SPME) — an alternative to DHS analysis is headspace solid-phase microextraction (HS-SPME). It is a simple, effective adsorption/desorption technique that integrates sampling, extraction, concentration, and sample introduction into a single step without the use of solvents (Contini and Esti, 2006). It is composed of a fused-silica fiber coated with different stationary phases (Cavalli et al., 2003), such as divinylbenzene (DVB), carboxen (CAR), polydimethylsiloxane (PDMS), carbowax (CW), and their combinations (Cavalli et al., 2004).

   It is a low-cost alternative to P/T and DHS systems with the versatility of a syringe. The main advantage of SPME is its reduced sample manipulation and simplicity, so extraction times are reduced and possess little risk of cross-contamination between samples compared to P/T methods (Kalua et al., 2006). Depending on the fiber, it also offers acceptable repeatability and a good linearity (Cavalli et al., 2003). In a comparative study with P/T methods, SPME was found to be advantageous for the analysis of volatiles associated with olive oil quality (Kanavouras et al., 2005) due to shorter sampling times and simpler procedures.

   However, the SPME method has limitations that include difficulties in inter-fiber comparisons and diagnosis of fiber performance and death. The lack of fiber comparativeness may limit the use of SPME in long-term experiments that might require change of fibers within an experiment (Kalua et al., 2006).

Since the 1980s, many works have been published on the utilization of chromatographic technique to analyze olive oil flavor by the use of different olive oil volatile compounds pre-extraction methods. Table 2 summarizes the chromatographic techniques applied to olive oil sector from 1980 to the present. Particular attention has been devoted to the olive oil volatile compounds extraction and concentration techniques and separation and identification methods applied.

SUMMARY

The gas chromatographic technique has been widely applied to olive oil sensory evaluation since 30 years ago due to its advantages: it needs small amounts of sample with little preparation, it is a fast analysis with high precision and resolution, and it can be coupled to other techniques, e.g., mass spectrometry.

An olive oil aroma analysis by GC method needs a previous volatile compounds extraction and concentration technique, because they are present at very low concentrations. P/T on activated charcoal, as adsorbent, was the principal method used in the 1980s, but from the beginning of the 1990s the DHS on Tenax adsorbent was widely used for this purpose.

However, SPME has been the technique most commonly applied to extract and concentrate olive oil volatile organic compounds. Different polymers have been utilized as adsorbents, but PDMS and the combination of DVB/CAR/PDMS have been the preferred fibers used from the beginning of the 21st century to the present.

Regarding the of VOCs, separation and identification of VOCs, different columns have been utilized, such as Chromosorb, Supelcowax, Carbowax, or DB-Wax, although the first one was mainly used in the 1980s. The great majority of the works studied have been applied FID detector.

TABLE 2
Applications of Chromatographic Method to Olive Oil Aroma Evaluation

Ref.	VOCs extraction and concentration method	VOCs separation and/or identification method	Aim of the work
(Olías et al., 1977)	P/T (activated charcoal)	Chromosorb P (30% Carbowax 20 M) in GLC-FID/MS	Analysis of VOCs in the aroma of a VOO
(Olías et al., 1978)	P/T (activated charcoal)	Chromosorb P (30% Carbowax 20 M) in GLC-FID/MS	Study the aroma composition of two olive oils from different provenance
(Dobarganes et al., 1980)	P/T (activated charcoal)	Chromosorb P (5% Carbowax 20 M) in GLC-FID	Study VOCs of VOO aroma
(Olías et al., 1980)	P/T (activated charcoal)	Chromosorb P (5% Carbowax 20 M) in GLC-FID/MS	VOCs evolution in the olive oil aroma, during the ripening process on samples of Picual and Hojiblanca
(Del Barrio et al., 1981)	SHS	Chromosorb P (30% Carbowax 20 M) in GLC-FID	Analysis of VOCs of fusty olive oils
(Gutiérrez et al., 1981)	P/T (activated charcoal)	Chromosorb WAW in GLC-FID/MS	Identification of the VOCs in the olive oil aroma obtained from fusty fruits
(Dobarganus et al., 1986)	P/T (activated charcoal)	Chromosorb WAW (30% Carbowax 20 M) in GC-FID/MS	Relationship between the composition of VOO and the VOCs produced during thermal-oxidation
(Solinas et al., 1987)	P/T (activated charcoal)	GLC and HPLC	Relationship between the autoxidation products of oils and the rising of rancidity in organoleptic evaluation
(Yoo et al., 1988)	High-vacuum cold finger distillation	Supelcowax-10 column in a GC-FID/MS	Analysis of the volatiles produced from olive oil by heat
(Morales and Aparicio, 1993)	DHS (Tenax TA)	Fused-silica Supelcowax 10 capillary column in a GC-FID	Characterizing some European olive oil varieties by volatiles
(Morales et al., 1994)	DHS (activated charcoal)	Fused-silica capillary column OV-1 in a GC/MS	Study the biogenesis of the compounds that contribute to green odor notes of VOO aroma
(Olías et al., 1993)	DHS (Tenax TA)	Fused-silica Supelcowax 10 capillary column in a GC-FID	Determination of VOCs in VOO
(Morales et al., 1995)	DHS (Tenax TA)	Supelcowax 10 capillary column in a GC-FID/MS	Relationships between the sensory attributes produced by the whole VOO matrix and its VOCs
(Angerosa et al., 1996)	DHS (activated charcoal)	Carbowax 20 M column in HRGC	Determination of the metabolites correlated with the fusty olive oil defect
(Aparicio et al., 1996)	DHS (Tenax TA)	DB-wax fused-silica Supelcowax 10 capillary column in a GC-FID/MS	Analysis of the relationship between the sensory attributes produced by the whole VOO matrix and its VOCs
(Di Giovacchino et al., 1996)	DHS (activated charcoal)	HRGC	Measurement of the effects of mixing leaves with olives on the chemical and organoleptic properties
(Aparicio et al., 1997)	DHS (Tenax TA)	DB-wax fused-silica Supelcowax 10 capillary column in a GC-FID/MS	Study the sensory and chemical authentication of the most marketed VOO varieties

(Morales et al., 1997)	DHS (Tenax TA)	DB-wax fused-silica capillary column in GC/MS	Study the changes produced in the initial content of VOO and in its sensory characteristics during oxidation
(Williams et al., 1997)	DHS (Tenax TA)	Supelcowax 10 capillary column in a GC/MD	Identification of the olive oil VOCs which possess organoleptic properties
(Aparicio and Morales, 1998)	DHS (Tenax TA)	DB-wax fused-sílica column in GC/MS	Characterization of olive ripeness by green aroma compounds of VOO
(Angerosa et al., 1998)	DHS (activated charcoal)	Carbowax 20 M column in a GC-FID/MS	Characterization of seven new hydrocarbon compounds present in the aroma of VOO
(Angerosa et al., 1998)	DHS (activated charcoal)	Carbowax 20 M column in a GC-FID/MS	Detection of olive oil VOCs formed at crushing and at different malaxation times
(Morales et al., 1998)	SFE system / DHS (Tenax TA)	DB-wax fused-silica capillary column in a GC-FID/MD	Analysis of VOO aroma by SFE
(Ruiz del Castillo et al., 1998)	DHS (Tenax TA)	Homemade chiral column in a GC-FID/RPLC	Detection of adulterations of hazelnut oil in olive oil
(Angerosa et al., 1999)	DHS	Silica capillary Carbowax 20 M column in HRGC	Determination of changes of the composition of C6 aldehydes, alcohols, and esters from the LOX pathway due to exclusively to the varietal factor
(Morales et al., 1999)	DHS (Tenax TA and Thermotrap)	Fused-silica DB-wax column in a GC-FID/MD	Importance of temperature and time during malaxing process on the production of C_5 and C_6 VOCs
(Morales et al., 1999)	DHS (Tenax TA)	Fused-silica DB-wax column in a GC-FID/MD	Effect on extraction conditions on sensory quality of VOO
(Ranalli et al., 1999)	P/T (activated charcoal)	Carbowax 20 M capillary column in a HRGC	Analysis of VOO composition of first and second extraction
(Angerosa et al., 2000)	P/T (activated charcoal)	Nordion silica capillary Carbowax 20 M column in a GC-FID/MD	Exploration of the relationships between green attributes of VOO and polyphenols and VOCs produced by lipoxygenase pathways
(Koprivnjak et al., 2000)	DHS	GC/MS	Change in the volatile components of VOO during fruit storage in aqueous media
(Bentivenga et al., 2001)	SHS-SPME	Phenomenex Zebron ZB-5 MS capillary column in a GC/MD	Analysis of olive oil flavor
(Marcos et al., 2002)	HS autosampler	MS	Discrimination of non-adulterated VOO samples from adulterated ones
(Marcos et al., 2002)	HS autosampler	MS	Characterization monovariental VOO
(Servili et al., 2002)	SHS-SPME (65 μm CW/DVB)	GC/MS	Referring the influence of the blade crusher on the olive oil quality

(Continued on next page)

TABLE 2
Applications of Chromatographic Method to Olive Oil Aroma Evaluation (*Continued*)

Ref.	VOCs extraction and concentration method	VOCs separation and/or identification method	Aim of the work
(Cavalli et al., 2003)	SHS	GC-FID/MS	Comparison of different extraction methods for the characterization of volatile/semivolatile compounds from VOO
	SPME (100 μm of PDMS, 85 μm CAR/PDMS, 70 μm CW/DVB and 50/30 μm DVB/CAR/PDMS)	Fused-silica capillary column HP-1 in a GC/MD	
	HSSE with PDMS	GC (TDS)-FID/MS	
(Flamini et al., 2003)	SHS-SPME (100 μm PDMS)	HP-wax and HP-5 capillary columns in GC/MS	Analysis of VOCs from leaves, fruits and VOO
(Vichi et al., 2003)	SHS-SPME (100 μm of PDMS, 75 μm CAR/PDMS, 65 μm PDMS/DVB and 50/30 μm DVB/CAR/PDMS)	Supelcowax-10 and SPB-1 columns in a GC-FID/MS	Evaluation of the efficiency of SPME for the qualitative and semi-quantitative analysis of VOO aroma
(Vichi et al., 2003)	SHS-SPME (DVB/CAR/PDMS)	GC-FID/MS	Evaluation the modifications occurring in the volatile composition of VOO during oxidation
(Bogusz et al., 2004)	SPE and MSPD	DB5-MS column in a GC-MS	Separation and isolation of B(a)P extracted from olive oil
(Carbonell et al., 2004)	DHS by air and concentration in a Tedlar bag	Supel-Q Plot capillary column in a GC/MD	To identify and quantify VOCs produced by a virgin olive oil and "olive oil" heated to 180°C and 240°C
(Cavalli et al., 2004)	SHS-SPME (50/30 μm of DVB/CAR/PDMS)	Fused-silica capillary columns in a GC-FID/MS	Comparison of different French and Spanish olive oil samples by the characterization of their VOCs
(García-González et al., 2004)	SHS: MPS and SPME (50/30 μm DVB/CAR/PDMS)	Capillary column TR-Wax in a GC-FID	Development a method based on a SAW-SPME technique to distinguish lampante from non-lampante VOO
(Jiménez et al., 2004)	SHS-SPME (100 μm PDMS)	HP 5 column in GC-FID	Characterization of olive oil defectives through the volatile aldehydes
(Peña et al., 2004)	DHS	MS	Classification of olive oil samples based on the concentration or BTEXs
(Tura et al., 2004)	SHS-SPME (100 μm a PDMS)	SGE DB-5 and a Phenomenex ZB-5 columns in a GC/MS	Varietal and processing effects on volatile profile of Australian VOO
(Zunin et al., 2004)	Gerstel TDS2 thermal extraction unit	GC/MD	Determination of the volatile composition of olive oils
(Dhifi et al., 2005)	P/T (activated charcoal)	Nordion silica capillary Carbowax 20 M column in a GC-FID/MS	Determination of volatile composition of olive oils from Tunisian cultivars

(Kanavouras et al., 2005)	DHS using Carbotrap-300 and Tenax TA as traps SHS-SPME (100 μm PDMS and 65 μm PDMS/DVB)	Fused-silica SPB-5 capillary column in a GC (TDS)/ITMS Fused-silica HP-5 capillary column in GC-TOFMS	Evaluation of the efficiency of DHS-TDS and SPME analytical techniques, in the analysis of VOC of olive oil
(Morales et al., 2005)	DHS (Tenax TA)	Fused-silica DB-wax column in a GC (TDS)-FID/MD	Determination of VOC responsible for VOO sensory defects
(Arrebola et al., 2006)	HS	GC/MS	Determination of polycyclic aromatic hydrocarbons in olive oil
(Baccouri et al., 2006)	SPME	GC/MS	Application of SPME to the analysis of VOCs of VOO
(Contini and Esti, 2006)	SHS-SPME (65 μm PDMS/DVB)	AT-wax column in GC	Evaluation of the possible effects of the matrix volatile composition on the quantitative determination of the VOC tested
(García-González et al., 2006)	SHS-SPME (50/30 μm DVB/CAR/PDMS)-MPS	SAW detector	Analysis of VOO aroma by a sensor system based on SAW with a preconcentration of VOC by SPME
(Jiménez et al., 2006)	SHS-SPME (100 μm PDMS, 65 μm CW/DVB and 75 μm PDMS/DVB)	HP 5 column in GC-FID	Analysis the viability of SPME to rapid discrimination "at-line" in the oil mill between olive oils
(Kalua et al., 2006)	SHS-SPME (50/30 μm PDMS/CAR/DVB)	SGE BPX5 column in GC	Development of a SHS-SPME/GC method for monitoring VOC in extended time-course experiments of VOO
(Luna et al., 2006)	DHS (Tenax TA)	Fused-silica DB-wax column in a GC-FID/MD	Characterization of varietal VOO, cultivated in an orchard, by quantification of the VOCs present in their aroma
(López-Feria et al., 2007)	HS-MPS	MS	Quantification of sensory attributes of VOO
(Cunha et al., 2007)	SPE	GC/MS	Quatification of free and sterified sterols in VOO
(López-Feria et al., 2007)	HS-MPS	MS	Rapid determination of the quality of VOO
(López-Feria et al., 2008)	HS-MPS	MS	Discrimination of VOO by their sensory attributes
(Servili et al., 2008)	SPME	GC/MS	Characterization of VOO aroma
(Fu et al., 2009)	SPE	RRLC/ESITOFMS and ESI-ITMSN	Characterization of phenolic compounds in VOO
(Koprivnjak et al., 2009)	SPME (DVB/CAR/PDMS)	GC-FID	Influence of free fatty acids, sterols and phospholipids on volatile compounds in olive oil headspace
(López-Feria et al., 2009)	SPE	GC/MS	Multiclass pesticide control in VOO
(Pérez et al., 2009)	HS	GC/MS	Determination of filbertone in spiked olive oils
(Vaz-Freire et al., 2009)	SPME	GC-TOFMS	Comprehensive GC for fingerprint pattern recognition in olive oils
(García-González and Aparicio, 2010)	DHS (Tenax)	GC-FID/e-nose	Coupling e-nose to GC to analysis VOO

Abbreviations used in Table 2: CAR: carboxen; CW: carbowax; DHS: dynamic headspace; DVD: divinylbenzene; ESI-ITMSN: electrospray ion-trap multiple mass spectrometry; ESITOFMS: electrospray ion-trap multiple mass spectrometry; FID: flame ionisation detector; GC-TOFMS: gas-chromatography-time-of-flight mass spectrometry; GLC: gas-liquid chromatography; HRGC: high resolution gas chromatography; HS, headspace; HSSE: headspace sorptive extraction; ITMS: ion trap-mass spectrometry; MD: mass detector; MPS: multi-purpose sampler; MS: mass spectrometer; MSPD: matrix solid-phase dispersion; PDMS: polydimethylsiloxane; P/T: purgue and trap; RPLC: reversed-phase liquid chromatography; RRLC: Rapid-resolution liquid chromatography; SHS: static headspace; SFE: Supercritical Fluid Extraction; SPE: solid phase extraction; SPME: solid phase microextraction; TDS: thermal desorption system; VOCs: volatile organic compounds; VOO: virgin olive oil.

Finally, it is important to emphasize that GC coupled to mass spectometry (GC/MS) has been applied from the beginning of the 1980s to the present to olive oil volatile compounds evaluation.

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