

Analytical, Nutritional and Clinical Methods

Aromagrams – Aromatic profiles in the appreciation of food quality

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Abstract

In this review a new approach to the food aroma analysis using various instrumental techniques is described. In the last decade extensive studies have been performed concerning aroma profiles (called in this article ‘aromagrams’) of food products and beverages. Aromagram is characteristic or even individual fingerprint of the odour, obtained usually by chromatographic methods or electronic nose. Basing on the fact that each product has its own unique pattern of volatile components, it is possible to get desired information about organoleptic quality and health safety of the product by qualitative and quantitative comparison of aromagrams of different foodstuffs. Appearance of aromagrams and their usefulness depend on the assay method, particularly on the extraction step. The paper reviews the methods developed to analyse volatiles in food products basing upon their aroma profiles.

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1. Introduction

Quality, in its most general sense, is the ability to meet specific requirements. In production and food quality control, protection is of utmost importance, that is ensurance of the health and life of consumers by taking appropriate action at every stage of production and food distribution. For the consumer, in turn, organoleptic quality is equally important and often decisive in the purchase. Among the many organoleptic quality components such as colour, rheologic properties or packaging, the flavour takes a particular place, i.e. the odour and taste sensations received when eating. Thus the presence, contents and composition of volatile substances in food have a substantial influence on its quality. What is more – each product has a characteristic and unique composition of volatile components. The aroma of most food products consists of complicated mixtures, sometimes consisting of several hundred compounds. An analysis of odour – its identification and quantitative evaluation – can constitute a valuable source

of information on the health quality of food, which includes both the organoleptic quality and the consumer’s health safety.

2. Potentialities of using aromagrams in the valuation of food quality

Volatile substances can originate at every production stage from all food components. They are present in raw materials, they come into being intentionally or unintended during the technological process and they are also created during storage of food products. Already thousands of odorous compounds have been detected and still new ones are being identified (Czapski, Grajek, & Pospiech, 1999). Aroma profiles found in food are the result of a huge number of reactions occurring between components of food products. The character of the resulting aroma depends upon a number of factors: availability and structure of the reagents, participation of fat, aminoacids and saccharides, reaction conditions (temperature, duration, water activity, pH, oxygen level, etc.). The main sources of volatile substances, also including aromatic ones, are shown in Fig. 1.

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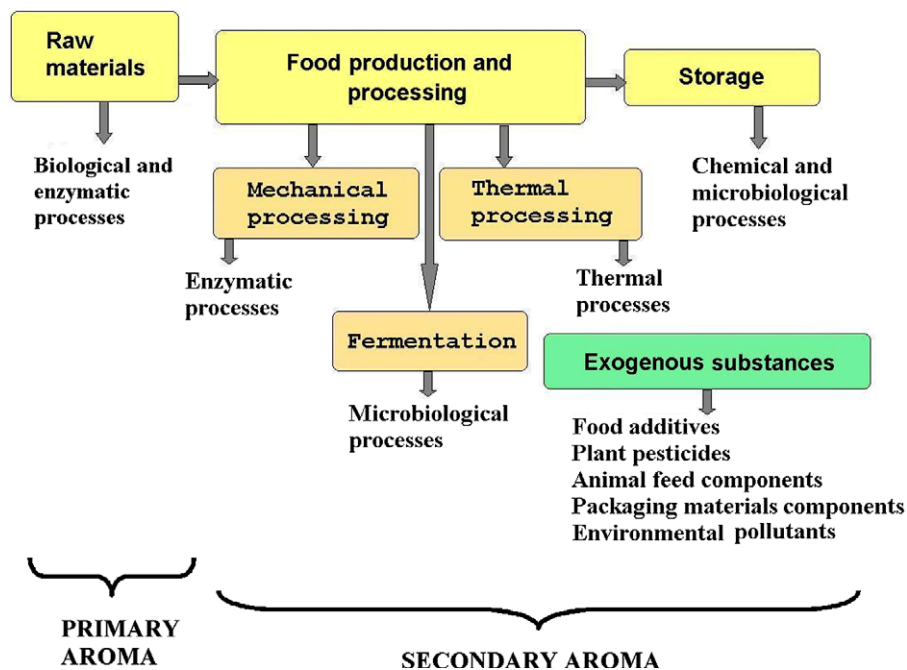


Fig. 1. Main sources of volatile food components.

2.1. Application of primary aroma profiles

Natural odorous compounds, for example those originating during metabolic pathways of aminoacids and fats – carboxylic acids, alcohols, carbonyl compounds, lactones – or during ripening of fruit – terpenes, esters, ethers – create the desired aroma of food (Grabowska, 1994). They are characteristic for a given raw material and product, but at the same time dependent upon a number of factors, in particular on the kind and origin of the raw material. Thus they can testify on the authenticity of a product. On the basis of determination of volatile components it is possible, among others, to detect adulterations of olive oil by other vegetable oils (Lorenzo, Pavón, Laespada, Pinto, & Cordero, 2002; Oliveros et al., 2002; Webster, Simpson, Shanks, & Moffat, 2000) or distinguish products depending on their geographical origin. So far there have been successfully elaborated methods for geographical differentiating such products as cheese (Bellesia et al., 2003), black tea (Borse, Rao, Nagalakshmi, & Krishnamurthy, 2002), fruit (Boudhrioua, Giampaoli, & Bonazzi, 2003), honey (Radovic et al., 2001; Soria, González, Lorenzo, Martínez-Castro, & Sanz, 2004), ham (Sánchez-Peña, Luna, García-González, & Aparicio, 2005), orange juice (Steine, Beaucousin, Siv, & Peiffer, 2001).

The composition of natural volatile elements of food, but also those originating during its processing is also a feature classifying food products. As an example, another composition will characterize brandy and another – whisky (Park, Kim, & Kim, 1999). Likewise – it is possible to state the brand of tea (Togari, Kobayashi, & Aishima, 1995) or coffee (Freitas, Parreira, & Vilas-Boas, 2001) on the basis of determining the type and number of essential compo-

nents. In scientific literature we find many reports on the subject of classification attempts and distinction of food products. Some of them, e.g. attempts on classifying of honeys depending on botanical origin are very promising the more so because up to now there are not any fast and reliable methods for such determinations in industrial practice (D'Arcy, Rintoul, Rowland, & Blackman, 1997; Guyot, Bouseta, Scheirman, & Collin, 1998; Guyot, Scheirman, & Collin, 1999).

2.2. Application of secondary aroma profiles

Numerous volatile compounds originating during production and processing of food may affect the health quality both positively and negatively. The qualitative and quantitative constitution of the originating composition depends strongly on the conditions of conducting the process and it is the result of a huge number of different, often not fully examined, enzymatic, microbiologic and thermal processes taking place in food (Janiček, Pokorný, & Davidek, 1977).

The determination of volatile substances can be thus exploited for the control of technological processes, e.g. to monitor the degree of oxidation of lipids in the production of powdered milk (Ulberth & Roubicck, 1995), in processing of vegetable oils (Stashenko, Puertas, Salgar, Delgado, & Martinez, 2000) or production of cooked meats (Brunton, Cronin, Monahan, & Durcan, 2000). Other example could be the determination of primary and secondary volatile products of saccharides and aminoacids conversions. Among these, the reactions of non-enzymatic browning – Maillard reactions – and the degradation of amino acids according to the Strecker mechanism in thermally processed food such as prunes and pumpkin seeds play the main roles

(Sabarez, Price, & Korth, 2000; Siegmund & Murkovic, 2004). Monitoring of thermal degradation of sulphur compounds – mainly aminoacids is an important indicator of quality in thermally treated meats (Farkaš et al., 1997). Likewise – changes taking place during thermal treatment of milk (Contarini & Povolo, 2002) or fruit and vegetable juices (Jia, Zhang, & Min, 1999; Servili, Selvaggini, Taticchi, Begliomini, & Montedoro, 2000) can be monitored using aroma profiles. In turn, determination of changes in the contents of volatile components such as aldehydes, organic acids and their esters, and alcohols in fermented beverages with fermentation performed in different ways and under various conditions can provide information important for the improvement and optimisation of the process (Apostolopoulou, Flouros, Demertzis, & Akrida-Demertzi, 2005; Bardi, Koutinas, Psarianos, & Kanellaki, 1997; Cortés, Gil, & Fernández, 2005; Ferreira et al., 1995; Hernández-Gómez, Úbeda, & Briones, 2003; Hernández-Gómez, Úbeda-Iranzo, Garcia-Romero, & Briones-Pérez, 2005; Madrera, Gomis, & Alonso, 2003b; Maicas, Gil, Pardo, & Ferrer, 1999; Mallouchos, Komaitis, Koutinas, & Kanellaki, 2002; Mallouchos, Komaitis, Koutinas, & Kanellaki, 2003a; Mateo, Jiménez, Pastor, & Huerta, 2001; Nonato, Carazza, Silva, Carvalho, & Cardeal, 2001; Patel & Shibamoto, 2002; Spranger et al., 2004; Torrea, Fraile, Garde, & Ancin, 2003; Tuszyński & Tarko, 2000; Valero, Moyano, Millan, Medina, & Ortega, 2002).

An important indicator of quality are volatile substances created during the storage of food. In the simplest case, during storage volatile flavour compounds escape and the gradual decay of flavour occurs. Most often, however, new aromatic substances also come into being, along mechanisms similar to those active in food processing, as the result of chemical or biochemical processes with the participation of microbial enzymes. A group of compounds having a positive effect on the organoleptic quality stands out here, i.e. components of the bouquet originating as the result of maturation of such articles as cheese and wines, but above all components of the bouquet coming into being in spoiled food – overdue, no more fresh and improperly stored. In most cases they are secondary products of lipid oxidation such as aldehydes, ketones, organic acids, hydrocarbons, appearing in a broad range of food products: oils (Cavalli, Fernandez, Lizzani-Cuvelier, & Loiseau, 2004; Vichi et al., 2003), meat (Andrés, Cava, & Ruiz, 2002), fish (Triqui & Bouchriti, 2003), crisps (Sanches-Silva, Lopez-Hernández, & Paseiro-Losada, 2005) or milk powder (Fenaille, Visani, Fumeaux, Milo, & Guy, 2003) (Fig. 2). Particularly disadvantageous, from the point of view of health quality, is the generation of aldehydes (Doleschall, Kemény, Recseg, & Kővári, 2001). Literature often points to hexanal as a component being an indicator of the degree of oxidation of food products. The relatively high concentration of hexanal and the observed rise in its

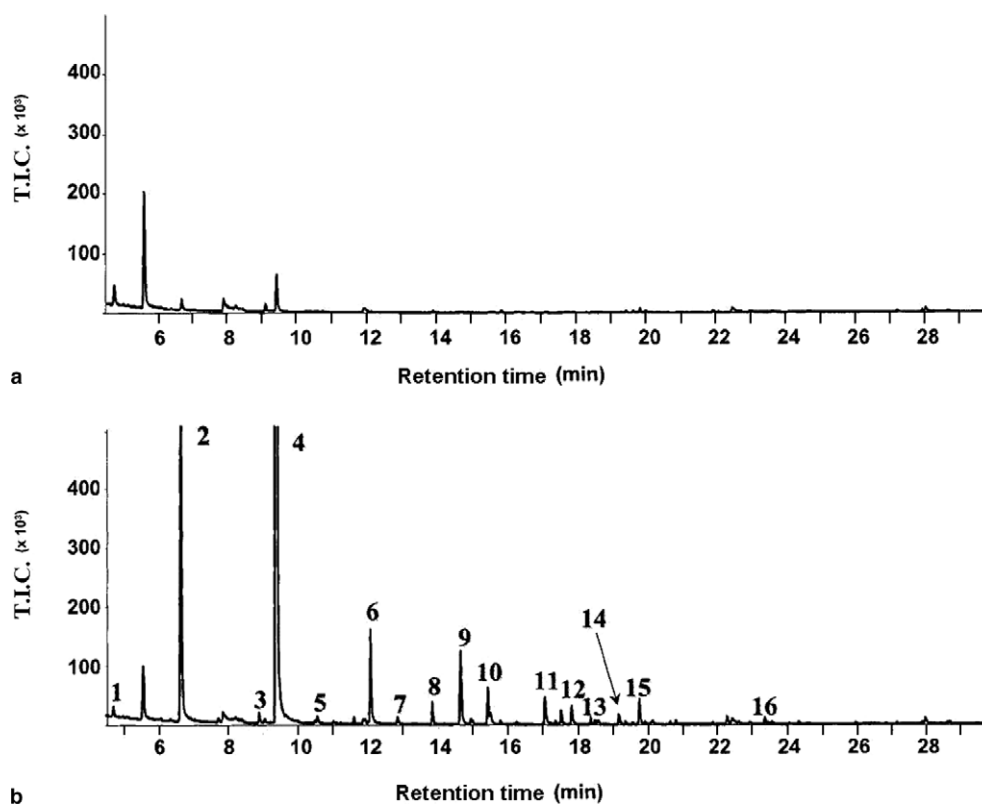


Fig. 2. Monitoring of the aroma profiles changes in infant formula, depending on different storage conditions, by using HS-SPME/GC-MS; (a) 3 weeks, 20 °C, stored under nitrogen, (b) 3 weeks, 37 °C, stored ungasged; 1 – 2-butanone, 2 – pentanal, 3 – 2,3-pentanedione, 4 – hexanal, 5 – 2-pentenal, 6 – heptanal, 7 – 2-hexenal, 8 – pentanol, 9 – octanal, 10 – 2-heptenal, 11 – nonanal, 12 – 2-octenal, 13 – 1-octen-3-ol, 14 – 2,4-heptadienal, 15 – benzaldehyde, 16 – 2,4-nonadienal (Reproduced from Fenaille et al., 2003).

concentration during storage as well as the low odour threshold indicate its suitability as a marker. Determination of changes in the content of hexanal is usable mainly in the evaluation of the quality of meat products (Andrés, Cava, Ventanas, Muriel, & Ruiz, 2004; Brunton et al., 2000; Carrasco, Tárrega, Ramirez, Mingoarranz, & Cava, 2005; Fernando, Berg, & Grün, 2003; Morcuende, Estévez, Ruiz, & Cava, 2003; Nielsen, Sørensen, Skibsted, & Bertelsen, 1997; Wong, O'Reilly, & Pawliszyn, 2004), but for vegetable oils such as olive oil it has been suggested that rather the determination of nonanal would be advisable, as in products of that type the significant amount of hexanal originates not only from chemical auto-oxidation of lipids but also from the enzymatic “lipoygenase pathway” (Vichi, Pizzale, Conte, Buxaderas, & López-Tamames, 2003).

In the course of a technological process or already during storage, food products can be infected and mould and putrefaction can take place. This causes, of course, significant deterioration of the organoleptic quality and health safety of food, which can be detected on the basis of changes observed in aroma profiles (Lyew, Gariépy, Raghavan, & Kushalappa, 2001; Marsili, 1999; Nakai et al., 1999; Ogihara, Horimoto, Wang, Skura, & Nakai, 2000). For instance, an indicator of the bacterial decay of fish giving the characteristic amine fishy odour is trimethylamine originating from the naturally occurring decomposition of trimethylamine oxide by bacterial enzymes (Triqui & Bouchriti, 2003). The infection by undesired microorganisms is also essential in forming the odour during fermentation processes – lactic and alcoholic fermentation. In aroma profiles were identified many compounds, which are indicators of microbiological infection of fermented products (Wasiak, 2000). For example, in raw spirits, the presence of an increased amount of butyl compounds, chiefly isobutyl alcohol but also ethyl butyrate and isobutyl propionate, may indicate infection by putrefactive bacteria (Kłosowski, Czupryński, Kotarska, & Wolska, 2003). Infection by acetic acid bacteria can lead to increased production of ethyl acetate and propanol during alcoholic fermentation and infection by lactic bacteria to increased production of ethyl lactate (Apostolopoulou et al., 2005).

Other numerous examples of the suitability of using aromagrams for the evaluation of food quality are presented in Table 1.

3. New trends in the determination of odorous substances in food products

A classic approach to the evaluation of organoleptic quality of food is based on the exploitation of sensoric analysis, i.e. analysis employing the use of taste, flavour, vision and touch senses, carried out by a group of properly trained estimators. Sensoric analysis can be a perfect tool in carrying out marketing tests of consumer preferences, but because of great human participation, it contains many limitations. Its basic shortcoming is low repeatability and

reproducibility of results connected to many subjective factors, such as sensoric susceptibility of the estimating person, state of health, comfort, adaptation or fatigue, or objective factors – conditions of carrying out the analysis. The specific character of sensoric analysis lies in the fact that it provides information on sensations perceived by human senses in the effect of complex chemical stimuli, and in this respect it is irreplaceable. Its great limitation, however, is the lack of possibility of identifying the compounds having an influence on aroma or flavour, including also components harmful to health, as well as lack of possibility to perform a quantitative analysis.

Because of these deficiencies of sensoric analysis methods, a perfect complement in the evaluation of organoleptic food quality is instrumental analysis. Appropriate instrumental techniques allow a detailed and complex qualitative and quantitative analysis of volatile components, which shape the flavour compositions of food products. The information obtained permits the characterization of products with respect to their classifying and also disqualifying features, such as harmfulness to health, falsification or foulness of a product. Among the many proposals and solutions provided, more and more applications are found by techniques based on the creation and separation of aromatic profiles, “aromagrams” of a kind characteristic for a given product (Fig. 3). In such an approach, the source of information is provided not only by single compounds, but also by mutual qualitative and quantitative relations taking place between components of the volatile fraction of the product. The comparison of profiles obtained from different products can in turn lead to the separation of single substances or groups of marker substances indicating differences between products of different origin or differing in quality. For example, the presence and condensation level of hexanal in the volatile fraction of a product is an indicator of the oxidation degree of lipid components and it can indicate lower quality or even foulness of the food product (Andrés et al., 2004; Brunton et al., 2000; Carrasco et al., 2005; Fernando et al., 2003; Morcuende et al., 2003; Nielsen et al., 1997; Sanchez-Silva, Quirós, López-Hernández, & Paseiro-Losada, 2004; Wong et al., 2004).

The techniques employed most often, allowing the creation and recognition of “aromagrams” are chromatographic techniques, in particular gas chromatography and so-called electronic noses.

3.1. Non-chromatographic techniques

Because they are easy to build and as they provide a short time of analysis, “electronic noses” are becoming more and more popular. These are circuits consisting of appropriately chosen non-specific electronic gas sensors of various affinity, built from such materials as metal oxides, organic polymers and quartz crystals or lithium niobate (Mielle, 1996). Similar to the human nose, the “artificial nose” recognizes rather a characteristic odour than singular compounds. The physical or chemical inter-

Table 1
Applications of “aromagrams” in food quality assessment

Food product	Analytes (major classes)/number of compounds determined	Potentialities of practical use	Techniques used	References
<i>Meat and fish products</i>				
Beef	Volatile metabolites produced by <i>Salmonellae</i>	Screening of bacterial contaminated food	HS-SPME/GC-FID	Ogihara et al. (2000)
Beef	Volatile compounds	Detection of vacuum-packed beef spoilage	Electronic nose	Blixt and Borch (1999)
Catfish	Geosmine, isoborneol	Assessment of fish organoleptic quality	SD/HS-SPME/GC-MS	Zhu et al. (1999)
Chicken meat	Hexanal	Detection of meat spoilage during storage	HS-SPME/GC-MS	Wong et al. (2004)
Cooked beef	Selected aroma compounds (aldehydes, furanes, ketones, nitrogen compounds, sulphur compounds)/36	Identification of key-odorants for the aroma of cooked meat	HS-SPME/GC-MS	Machiels and Istasse (2003)
Cooked pork	Aroma compounds (alcohols, aldehydes, furanes, hydrocarbons, ketones, nitrogen compounds, sulphur compounds)/95	Characterization of the product	HS-SPME/GC-MS	Elmore et al. (2000)
Cooked turkey	Hexanal, pentanal	Monitoring of changes caused by lipid oxidation taking place during thermal processing and storage	HS-SPME/GC-FID	Brunton et al. (2000)
Cured hams	Aroma compounds (alcohols, aldehydes, furanes, hydrocarbons, ketones, sulphur compounds)/87	Assessment and comparison of organoleptic quality of hams cured by the use of various methods	SDE and DHS/GC-MS	Dirinck et al. (1997)
Dried meats “cecinas”	Aroma compounds (acids, alcohols, aldehydes, esters, furanes, hydrocarbons, ketones, nitrogen compounds, phenols)/110	Characterization of products depending on animal species	DHS/GC-MS	Hierro et al. (2004)
Dry-cured ham	Aroma compounds (acids, alcohols, aldehydes, hydrocarbons, ketones, lactones, nitrogen compounds, sulphur compounds)/107	Monitoring of aroma changes taking place during ham ripening; identification of organoleptic quality markers	SPME/GC-MS	Andrés et al. (2002)
Dry-cured ham, canned liver sausage	Aroma compounds (acids, alcohols, aldehydes, hydrocarbons, ketones, terpenoids)/122	Organoleptic quality assessment	HS-SPME and SPME/GC-MS	Ruiz et al. (2001)
Dry-cured hams	Aroma compounds (alcohols, aldehydes, hydrocarbons, ketones)/30	Characterization of hams depending on their geographical origin and animal breed type; identification of markers indicating geographical and breed diversification	HS-SPME/GC-FID and GC-MS	Sánchez-Peña et al. (2005)
Dry-cured hams	Hexanal	Monitoring of lipid oxidation state during ham ripening depending on processing conditions	HS-SPME/GC-MS	Andrés et al. (2004)
Dry-cured loin	Aroma compounds (acids, alcohols, aldehydes, esters, furanes, hydrocarbons, ketones, nitrogen compounds, sulphur compounds, terpenoids)/133	Characterization of the product; investigation on the influence of breed type of swines and their diet on organoleptic properties of the product	HS-SPME/GC-MS	Muriel et al. (2004)
Dry-cured loins	Hexanal	Monitoring of organoleptic quality changes of vacuum-packed loins during storage depending on the animal diet and conditions of irradiation	HS-SPME/GC-MS	Carrasco et al. (2005)
Fish meat	Aroma compounds derived from lipid degradation (alcohols, aldehydes, ketones)/19	Organoleptic quality assessment	DHS/GC-MS	Refsgaard et al. (1999)
Hamburger, salmon	Volatile metabolites produced by <i>E. coli</i> and <i>S. aureus</i>	Detection of contamination of food with bacteria	DHS/GC-FID	Nakai et al. (1999)
Pork	Hexanal	Monitoring of lipid oxidation state in raw and thermal processed meat during storage	HS-SPME/GC-FID and GC-MS	Nielsen et al. (1997)
Pressure-cooked hen meat	Aroma compounds (sulphur compounds)/27	Identification of key-odorants for the aroma of cooked meat	HS-SPME/GC-MS HS-SPME/GC-FID SDE and SE/GC-FID, GC-O and GC-MS	Morcuende et al. (2003), Fernando et al. (2003) Farkaš et al. (1997)

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Table 1 (continued)

Food product	Analytes (major classes)/number of compounds determined	Potentialities of practical use	Techniques used	References
Sardine	Undesired odour compounds formed during storage (aldehydes, ketones)/24	Determination of fish freshness; identification of markers indicating state of fish freshness	SE and HS-SPME/GC-FID and GC-O	Triqui and Bouchriti (2003)
Sausages	Aroma compounds (acids, alcohols, aldehydes, esters, hydrocarbons, ketones)/90	Characterization of the product	HS-SPME/GC-MS	Marco et al. (2004)
Smoked hams	Nitrosoamines	Determination of nitrosoamines in hams	SD/HS-SPME/GC-TEA and GC-MS	Sen et al. (1997)
Swine fat	Volatile compounds	Assessment of meat organoleptic quality depending on animal diet	Electronic nose	González-Martin et al. (2000)
<i>Fruits</i>				
Apples	Selected aroma compounds (alcohols, esters)/19	Investigation on the influence of cultivation conditions on fruit quality	SE/GC-FID	Mpelasoka and Behboudian (2002)
Apples	Selected aroma compounds (esters)/29	Fast screening of fruits and vegetables quality	HS-SPME/GC-MS and DHS/GC-FID	Song et al. (1997)
Apples	Aroma compounds (alcohols, aldehydes, esters, hydrocarbons)/43	Investigation on the influence of crop time and storage conditions on fruit quality	SE/GC-FID and GC-MS	Girard and Lau (1995)
Apples	Selected aroma compounds (alcohols, aldehydes, esters)/25	Monitoring of changes in volatiles production depending on storage conditions	DHS/GC-MS	Argenta et al. (2004)
Apples	Selected aroma compounds (esters, terpenoids)/21	Comparison of quality of normal and scald-developing apples	HS-SPME/GC-MS	Paliyath et al. (1997)
Apples	Aroma compounds (alcohols, aldehydes, esters)/39	Investigation on the influence of 1-methylcyclopropen on volatiles production and fruit aroma during storage	HS-SPME/GC-MS	Lurie et al. (2002)
Bananas	Selected aroma compounds/15	Monitoring of aroma changes during storage (ripening) and drying, differentiation depending on geographical origin; identification of quality markers	HS-SPME/GC-FID, GC-MS and GC-O	Bouhrioua et al. (2003)
Cashew nuts	Hydrocarbons derived from lipid radiolysis	Identification of irradiated cashew nuts	SE/pLC/pTLC and SFE/GC-MS	Bhattacharjee et al. (2003)
Figs	Aroma compounds (alcohols, aldehydes, esters, hydrocarbons, terpenoids)/99	Characterization of the aroma of different figs varieties	DHS/GC-FID and GC-MS	Grison-Pigé et al. (2002)
Fruits (raspberries, strawberries, blackberries, banana, mango)	Natural aroma compounds and compounds formed during storage and processing (alcohols, esters, terpenoids)	Characterization and analysis of aroma changes during storage and processing of fruits	HS-SPME/GC-FID and GC-MS	Ibáñez et al. (1998)
Peaches, nectarines	Selected aroma compounds (alcohols, esters, lactones)/18	Assessment of fruit maturity, optimization of harvest date	DHS/GC-FID and GC-MS	Lavilla et al. (2002)
Peanuts	Selected aroma compounds /9	Investigation on the influence of water activity during storage of peanuts on their aroma changes	HS-SPME/GC-FID	Reed et al. (2002)
Pears	Volatile compounds/7	Studies on the differences of fruit aroma depending on storage conditions and maturity stage	Electronic nose and HS/GC-FID and GC-MS	Oshita et al. (2000)
Prunes	Selected volatile compounds derived from thermal degradation of carbohydrates taking place during Maillard reactions and caramelisation/9	Monitoring of quality changes during drying; identification of quality markers	HS-SPME/GC-MS	Sabarez et al. (2000)

Strawberries	Selected aroma compounds (aldehydes, esters)/22	Classification of strawberries depending on maturity stage and their variety	HS-SPME/GC/GC-FID	Williams et al. (2005)
Tropical fruits (cupuassu, cajá, siriguela, graviola)	Aroma compounds (alcohols, esters, terpenoids)	Characterization of fruits aromas	HS-SPME/GC-MS	Augusto et al. (2000)
<i>Vegetables</i>				
<i>Allium</i> hybrids	Sulphur aroma compounds	Comparison of hybrids and mother plants and characterization of their aromas	HS-SPME/GC-FID and GC-MS	Keusgen et al. (2002)
Fresh chilli	Selected aroma compounds/6	Studies on the differences of chilli aroma depending on maturity stage	HS-SPME/GC-MS	Mazida et al. (2005)
Iceberg lettuce	Undesired compounds formed during fermentation (alcohols, esters)/19	Monitoring of quality changes during storage depending on packaging conditions	HS-SPME/GC-MS	Smyth et al. (1998)
Onion	Sulphur aroma compounds	Characterization of the product	SE and HS-SPME/GC-MS	Arnault et al. (2000)
Potatoes	Volatile metabolites produced by pathogenic microorganisms	Detection of microbial infection of potatoes during storage	DHS/GC-FID	Lyew et al. (2001)
Pumpkin seeds	Volatile compounds derived from thermal degradation (alcohols, aldehydes, furanes, ketones, nitrogen compounds)/34	Monitoring of chemical changes during roasting of seeds	HS-SPME/GC-MS	Siegmund and Murkovic (2004)
Red paprika	Aroma compounds (alcohols, aldehydes, benzene derivatives, esters, hydrocarbons, ketones, naphthalene derivatives, nitrogen compounds, sulphur compounds, terpenes)/184	Identification of differences of sweet and pungent paprika aromas	SDE/GC-MS	Kocsis et al. (2002)
Rehydrated vegetables (beans, bell peppers, leeks)	Aroma compounds (aldehydes, ketones, sulphur compounds)/28	Assessment of sensory properties of rehydrated vegetables	DHS/GC-FID, GC-O and GC-MS	Ruth et al. (1995)
Tomatoes	Volatile compounds/10	Monitoring of aroma changes during storage and classification depending on tomato variety	Electronic nose, HS-SPME/GC-MS	Berna et al. (2004)
<i>Oils</i>				
Olive oil	n-alkanes	Detection of adulteration with vegetable oils	pLC/GC-FID	Webster et al. (2000)
Olive oil	Volatile compounds	Detection of adulteration with vegetable oils	Electronic nose HS/MS	Oliveros et al. (2002) Lorenzo et al. (2002)
Olive oil	Volatile impurities (benzene, ethylbenzene, styrene, toluene, xylenes)	Detection of volatile impurities in oils	HS/MS	Peña et al. (2004)
Olive oil	Aroma compounds (alcohols, aldehydes, esters, ketones)/50	Characterization of the product	DHS and HS-SPME/ GC-FID and GC-MS	Kanavouras et al. (2005)
Olive oil	Aroma compounds (alcohols, aldehydes, hydrocarbons, terpenoids)/22	Characterization of the product	TD/GC-MS	Zunin et al. (2004)
Olive oil	Aroma compounds (alcohols, aldehydes, esters, hydrocarbons, ketones, terpenoids)/102	Characterization of the product	HS-SPME/GC-FID and GC-MS	Vichi et al. (2003)
Olive oil	Selected aroma compounds (alcohols, aldehydes, esters, hydrocarbons, ketones)/50	Assessment of the health quality of olive oil depending on producing; optimization of producing conditions	HS-SPME/GC-MS	Servili et al. (2003)
Olive oil	Aroma compounds/15	Investigation on the aroma profile changes depending on olive variety and technological process conditions	HS-SPME/GC-FID and GC-MS	Tura et al. (2004)
Olive oil	Compounds derived from lipid degradation (alcohols, aldehydes, furanes, hydrocarbons, terpenoids)	Monitoring of rancidity state of olive oils during storage; identification of quality markers	HS-SPME/GC-FID and GC-MS	Vichi et al. (2003), Cavalli et al. (2004)

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Table 1 (continued)

Food product	Analytes (major classes)/number of compounds determined	Potentialities of practical use	Techniques used	References
Olive oil	Volatile aldehydes derived from lipid oxidation	Differentiation of olive oils made of raw materials of proper or improper quality	HS-SPME/GC-FID	Jiménez et al. (2004)
Sunflower oil	Volatile aldehydes derived from lipid oxidation	Monitoring of changes in sensory characteristic of oils during refining and storage; identification of markers indicating oxidation state of oils	HS and HS-SPME/GC-FID	Doleschall et al. (2001)
Sunflower oil	Volatile aldehydes derived from lipid oxidation	Monitoring of changes in sensory characteristic of oils during thermal processing	HS-SPME/GC-ECD	Stashenko et al. (2000)
Vegetable oils	Volatile compounds	Classification of vegetable oils	Electronic nose	Martin et al. (1999), Martin et al. (2001)
Vegetable oils	Volatile impurities (benzene, ethylbenzene, halogenated derivatives, styrene, toluene, xylenes)/37	Detection of volatile impurities in oils	HS-SPME/GC-MS	Page and Lacroix (2000)
Vegetable oils	Aroma compounds (acids, alcohols, aldehydes)/30	Classification of oils depending on their origin and rancidity state	Electronic nose and HS-SPME/GC-MS	Biswas et al. (2004)
Vegetable oils	Aroma compounds (alcohols, aldehydes, hydrocarbons)/60	Classification of oils depending on their origin and rancidity state	HS-SPME/GC-FID and GC-MS	Mildner-Szkudlarz et al. (2003)
<i>Dairy products</i>				
Butter	Aroma compounds (acids, alcohols, aldehydes, esters, ketones)/48	Monitoring of organoleptic quality during storage in different temperatures	DHS and HS-SPME/GC-MS	Povolo and Contarini (2003)
Camembert-type cheeses	Bouquet components (acids, alcohols, chlorine compounds, esters, hydrocarbons, ketones, sulphur compounds)/70	Fast assessment of cheeses quality	HS-SPME/MS and HS-SPME/GC-MS	Pérès et al. (2001)
Camembert-type cheeses	Bouquet components (acids, alcohols, aldehydes, chlorine compounds, esters, hydrocarbons, ketones, sulphur compounds, terpenoids)/96	Fast assessment of cheeses quality	DHS/MS and DHS/GC-MS	Pérès et al. (2002)
Camembert-type cheeses	Bouquet components/12	Fast assessment of cheeses quality	HS/MS and HS/GC-MS	Pérès et al. (2002)
Cheeses	Bouquet components (acids, benzene derivatives, esters, furanes, ketones, lactones, nitrogen compounds, sulphur compounds, terpenoids)/73	Characterization of various types of cheeses, identification key-odorants for their aroma	HS-SPME/GC-O, GC-FID and GC-MS	Frank et al. (2004)
Cheeses	Bouquet components (acids, ketones, lactones)/27	Characterization and classification of cheeses depending on their type and origin	SDE/GC-MS	Dirinck and Winne (1999)
Emmental-type cheeses	Bouquet components produced by <i>Propionibacterium</i> (acids, alcohols, aldehydes, esters, ketones)/74	Investigation on the influence of <i>Propionibacterium</i> on organoleptic quality of cheese	DHS/GC-MS and SE/GC-FID	Thierry et al. (2004)
Feta-type cheese	Bouquet components (alcohols, aldehydes, esters, hydrocarbons, ketones)/54	Studies on the influence of various bacterial cultures and yeast strains on cheese aroma	DHS/GC-MS	Bintsis and Robinson (2004)
Infant formula	Volatile compounds derived from lipid oxidation/16	Early detection of lipid oxidation in milk powder during storage; identification of markers indicating oxidation state of the product	HS/MS and HS-SPME/GC-MS	Fenaille et al. (2003)
Milk	Aroma compounds formed during thermal processing (aldehydes, ketones)/11	Classification of milk depending on type of heat treatment used; identification markers indicating type of heat treatment used	DHS/GC-FID and HS-SPME/GC-MS	Contarini and Povolo (2002)
Milk	Aroma compounds	Differentiating of milks of proper or improper quality caused by various factors (light or temperature activity, presence of copper, bacterial contamination)	HS-SPME/MS	Marsili (1999)

Milk powder	Aldehydes derived from lipid oxidation	Monitoring of flavor defects caused by lipid oxidation	SD/HS/GC-FID and GC-MS	Ulberth and Roubicck (1995)
Parmezan-type cheeses	Bouquet components (acids, alcohols, aldehydes, esters, ketones) /35	Differentiating of products depending on their producer, geographical origin and time of ripening	DHS and HS-SPME/GC-MS	Bellesia et al. (2003)
Sheep cheese	Volatile metabolites produced by microorganisms (acids, alcohols, esters, ketones)/31	Characterization of bouquet depending on composition of microorganisms used in cheese production	HS-SPME/GC-FID	Dahl et al. (2000)
Whey protein concentrate	Aroma compounds (acids, aldehydes, hydrocarbons, ketones)/43	Assessment of organoleptic quality of concentrate before using in food production	HS-SPME/GC-MS	Quach et al. (1999)
<i>Juices</i>				
Apple juice	Selected aroma compounds (alcohols, aldehydes, esters)/20	Assessment of the quality of juices depending on storage conditions of fruit	HS and LLE/GC-FID	Dixon and Hewett (2001)
Apple juice	Volatile metabolites produced by microorganisms /16	Assessment of microbiological quality of juices	HS-SPME/GC-MS	Zierler et al. (2004)
Orange juice	Selected volatile compounds (alcohols, aldehydes, esters, terpenoids)/25	Differentiating of juices depending on kind of treatment (pasteurization, reconstitution from the concentrate)	Electronic nose and HS/GC-FID	Shaw et al. (2000)
Orange juice	Selected aroma compounds/8	Studies on aroma changes depending on method of treatment and processing conditions	HS-SPME/GC-FID	Jia et al. (1999)
Orange juice	Volatile compounds	Differentiating of juices depending on geographical origin of fruit	Electronic nose	Steine et al. (2001)
Orange juice	Selected aroma compounds/17	Characterization of the product	HS-SPME/GC-FID	Steffen and Pawliszyn (1996)
Tomato juice	Aroma compounds (acids, alcohols, aldehydes, esters, ethers, furanes, hydrocarbons, ketones, phenols, sulphur compounds, terpenoids)/119	Optimization of thermal treatment parameters	HS-SPME/GC-MS	Servili et al. (2000)
<i>Alcoholic beverages</i>				
“Fino” wine	Bouquet components (acids, alcohols, esters)/34	Characterization of the product	LLCE and HS-SPME/GC-FID and GC-MS	Castro et al. (2004)
“Muoro” spirits	Bouquet components (acids, alcohols, esters)/28	Characterization of the product	DI and LLE/GC-FID	Souffleros et al. (2004)
Alcoholic beverages	Organic acids	Characterization of the product	SPE/HPLC-FD	Nascimento et al. (2000)
Alcoholic beverages	Volatile carbonyl compounds	Characterization and assessment of alcoholic beverages quality	HS-SPME/GC-ECD	Wardencki et al. (2003)
Beer	Sulphur compounds	Determination of volatile and semi volatile sulphur compounds in beer	HS-SPME/GC-FPD	Hill and Smith (2000)
Beer	Selected bouquet compounds (acids, alcohols, esters)/19	Characterization of the product	HS-SPME/GC-FID and GC-MS	Liu et al. (2005)
Beer	Selected alcohols and fatty acids esters/11	Characterization of the product	HS and HS-SPME/GC-FID	Jeleń et al. (1998)
Brandy, whisky	Organic acids	Classification of alcoholic beverages	SPE/GC-FID and GC-MS	Park et al. (1999)
Calvados, cognac	Bouquet components (acids, alcohols, aldehydes, benzene derivatives, esters, furanes, phenols, sulphur compounds, terpenoids)/331	Characterization and classification of alcoholic beverages	LLE, pGC and pLC/GC-MS	Ledauphin et al. (2004)
Champagne	Selected bouquet components/14	Studies on aroma changes caused by photodegradation	HS-SPME/GC-MS	D’Auria et al. (2003)
Cider brandy	Furanes, phenols	Investigation on the influence of technological process conditions on forming furanes and phenols	DI/HPLC-DAD	Madrera et al. (2003b)

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Table 1 (continued)

Food product	Analytes (major classes)/number of compounds determined	Potentialities of practical use	Techniques used	References
Cider brandy	Selected aroma compounds (acids, alcohols, aldehydes, esters)/32	Investigation on the influence of technological process conditions on bouquet of alcoholic beverages	DI and ME/GC-FID and GC-MS	Madrera et al. (2003b)
Cognac	Bouquet components (acids, alcohols, esters, terpenoids)/150	Identification of key-odorants for aroma of alcoholic beverages	DI and LLE/GC-O, GC-FID and GC-MS	Ferrari et al. (2004)
Cognac, whisky	Organic acids, phenols	Assessment of age and maturity stage of alcoholic beverages	SPE/GC-MS	Ng et al. (2000)
Grape marcs “Bagaceira”	Selected aroma compounds (acids, alcohols, esters)/33	Characterization of the product	DI and LLE/GC-FID	Silva et al. (1996)
Grape spirits	Volatile organic acids	Investigation of the influence of time of ripening and refining on organoleptic quality of alcoholic beverages	SPE/GC-FID	Diéguez et al. (2002)
Grape spirits “Orujo”	Aroma compounds (alcohols, aldehydes, esters)/31	Comparison of bouquets of alcoholic beverages from industrial and homemade sources	DI/GC-FID and GC-MS	Cortés et al. (2005)
Grape spirits “Orujo”	Selected aroma compounds (norisoprenoids, terpenes)	Classification of alcoholic beverages depending on grape variety, identification characteristic compounds for the given class	SPE/GC-FID and GC-MS	Diéguez et al. (2003)
Grape spirits “Tsipouro”	Selected bouquet compounds/10	Comparison of bouquets of alcoholic beverages from industrial and homemade sources	DI and LLE/GC-FID and GC-MS	Apostolopoulou et al. (2005)
Grape wine	Volatile compounds derived from fermentation (acids, alcohols, esters)/28	Monitoring and comparison of wine fermentation processes depending on temperature of the process and use of immobilized or free yeast cell systems	LLE/GC-MS	Mallouchos et al. (2003a)
Grape wine	Volatile metabolites produced by <i>Saccharomyces Cerevisiae</i> /13	Monitoring of volatiles production during fermentation conducted with the use of yeast immobilized on grape skins	HS-SPME/GC-FID and GC-MS	Mallouchos et al. (2003a)
Grape wine	Bouquet components (acids, alcohols, esters)/33	Characterization of the product	HS-SPME/GC-FID and GC-MS	Baptista et al. (2001)
Grape wine	Volatile compounds	Differentiation of various sorts of wine	Electronic nose	Penza and Cassano (2004a, 2004b) Guadarrama et al. (2000) Guadarrama et al. (2001)
Grape wine	Bouquet components (alcohols, esters)/35	Differentiation of various sorts of wine	HS-SPME/GC-MS	Marengo et al. (2001)
Grape wine	Bouquet components (acids, alcohols, esters)/23	Characterization and differentiation of various sorts of wine	Electronic nose and LLE/GC-FID and GC-MS	Santos et al. (2004)
Grape wine	Fatty acids ethyl esters, acetic acid esters	Monitoring of changes in esters production during wine fermentation	HS-SPME/GC-MS	Vianna and Ebeler (2001)
Grape wine	Selected volatile compounds derived from fermentation/11	Studies on of spontaneous fermentation products in different musts and their influence on wine bouquet	DI/GC-FID	Clemente-Jimenez et al. (2004)
Grape wine	Selected higher alcohols and fatty acid esters/34	Investigation on the influence of must aeration before fermentation on production and composition of fusel oils and esters	LLCE/GC-FID	Valero et al. (2002)
Grape wine	Selected higher alcohols and fatty acid esters /12	Investigation on the influence of nitrogen contents in must on production and composition of fusel oils and esters depending on yeast strain	DI and LLE/GC-FID	Torrea et al. (2003)

Grape wine	Volatile compounds	Detection of wine adulteration with methanol, ethanol and other wines	Electronic nose	Penza and Cassano (2004a, 2004b)
Grape wine	Volatile metabolites produced by <i>Saccharomyces Cerevisiae</i> /13	Monitoring and comparison of volatiles production during fermentation conducted with the use of immobilized or free yeast cell systems	HS-SPME/GC-FID and GC-MS	Mallouchos et al. (2002)
Grape wine	Volatile metabolites produced by different strains of <i>Saccharomyces Cerevisiae</i> (acids, alcohols, esters)/53	Studies on differences in wine bouquets depending on yeast strain used	pLC/GC-FID and GC-MS	Patel and Shibamoto (2002)
Grape wine	Volatile metabolites produced by different strains of <i>Saccharomyces Cerevisiae</i> (acids, alcohols, esters)/30	Studies on differences in wine bouquets depending on yeast strain used	LLCE/GC-FID and GC-MS	Mateo et al. (2001)
Grape wine "Ruché"	Bouquet components (terpenoids)/59	Characterization of the product, studies on mechanisms of aroma components forming during fermentation	LLE and HS-SPME/GC-MS	Bonino et al. (2003)
Lemon liquors "Limoncello"	Selected aroma compounds (terpenoids)/31	Identification of key-odorants for assessment of the quality of alcoholic beverages	LLE/GC-FID and GC-MS	Versari et al. (2003)
Melon fruit spirits	Selected bouquet compounds/10	Studies on bouquet composition depending on fermentation conditions and distillation method	DI/GC-FID	Hernández-Gómez et al. (2003)
Melon fruit spirits	Bouquet compounds (acids, alcohols, aldehydes, esters)/58	Studies on bouquet composition depending on fermentation conditions and distillation method	DI/GC-FID and GC-MS	Hernández-Gómez et al. (2005)
Orange spirits	Bouquet components (alcohols, aldehydes, esters, terpenoids)/40	Characterization of the product	DI and HS-SPME/GC-FID and GC-MS	Porto et al. (2003)
Red grape wine	Bouquet components (acids, alcohols, esters, lactones, phenols, sulphur compounds, terpenoids)/69	Differentiating of wines of the same sort but derived from different vineyards	SPE/GC-FID, GC-O and GC-MS	Ferreira et al. (2001)
Red grape wine	Volatile compounds derived from fermentation (acids, alcohols, esters)/30	Investigation on the influence of lactic bacteria addition during fermentation on wine bouquet	LLCE/GC-FID and GC-MS	Maicas et al. (1999)
Red grape wine	Bouquet components (acids, alcohols, esters, terpenoids)/75	Characterization and classification of bouquet of wines produced from different grape varieties	SPE/GC-FID and GC-MS	Boido et al. (2003)
Red grape wine	Bouquet components	Classification of bouquet of wines produced from different grape varieties	Electronic tongue	Legin et al. (2003)
Red grape wine	Bouquet components (alcohols, esters)/15	Differentiation of wines depending on production technology used	LLE/GC-FID and GC-MS	Spranger et al. (2004)
Red wine	Chloroanisoles	Determination of contents of chloroanisoles originated from cork taint, studies on their influence on aroma	HS-SPME/GC-ECD	Martinez-Uruñuela et al. (2004)
Rum	Fatty acids ethyl esters	Characterization of the product	HS-SPME/GC-FID	Pino et al. (2002)
Sugar cane spirits "Cachaça"	Bouquet components (acids, alcohols, esters, hydrocarbons, terpenoids)/38	Comparison of bouquets of wines from industrial and homemade sources	HS-SPME and LLE/GC-FID and GC-MS	Nonato et al. (2001)
Tequila	Bouquet components (esters)/21	Differentiation of different brands of tequila	HS-SPME and SPME/GC-FID and GC-MS	Vallejo-Cordoba et al. (2004)
Whisky	Bouquet components (esters)/44	Characterization of the product	SPME, HS-SPME and SBSE/GC-MS	Demyttenaere et al. (2003)
White grape wine	Bouquet components (acids, alcohols, furanes, ketones, terpenoids)/59	Characterization and classification of wines depending on bouquet composition differences	LLCE/GC-MS	Rocha et al. (2000)
White grape wine	Bouquet components (acids, esters, phenols, sulphur compounds, terpenoids)/38	Characterization and classification of wines depending on bouquet composition differences	LLE/GC-FID, GC-FPD and GC-MS	Falqué et al. (2002)

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Table 1 (continued)

Food product	Analytes (major classes)/number of compounds determined	Potentialities of practical use	Techniques used	References
White grape wine	Bouquet components (acids, alcohols, esters, terpenoids)/33	Characterization and classification of wines depending on bouquet composition differences	SPME and HS-SPME/GC-MS	Demyttenaere et al. (2003)
White grape wine	Bouquet components (acids, alcohols, esters, furanes, phenols, sulphur compounds, terpenoids)/44	Characterization of the product	LLE, LLE/pLC and HS/GC-MS	Guth (1997)
White grape wine	Selected hexacarboxylic bouquet components (alcohols, aldehydes)	Investigation on the influence of production conditions on C6 aldehydes and alcohols contents	SD/GC-FID	Ferreira et al. (1995)
White wine	Fatty acids esters	Determination of esters in wines	HS-SPME/GC-FID	Rodriguez-Bencomo et al. (2002)
Wine	Volatile phenols	Determination of volatile phenols in wines	HS-SPME/GC-FID and GC-MS	Mejias et al. (2003)
Wine	3-alkyl-2-metoxypyrazines	Determination of 3-alkyl-2-metoxypyrazines in wines	HS-SPME/GC-NPD	Sala et al. (2000);
Wine	Bouquet components (acids, alcohols, esters, furanes, ketones, phenols, sulphur compounds)/47	Characterization of the product	SPE, ME and SPE/pLC/GC-FID, GC-O and GC-MS	Sala et al. (2002) Ferreira et al. (2002)
Wine	Terpenoids	Classification of different sorts of wines	HS-SPME and SPME/GC-MS	Garcia et al. (1998)
Wine	Volatile compounds derived from fermentation/6	Monitoring and comparison of fermentation depending on temperature of the process and use of immobilized or free yeast cell systems	DI/GC	Bardi et al. (1997)
Wine	Sulphur compounds	Assessment of organoleptic quality of wines	HS-SPME/GC-FPD	Mestres et al. (1998)
Wine	Volatile compounds	Characterization and classification of wines	PTR-MS	Boscaini et al. (2004)
Wine	Selected volatile compounds derived from fermentation /6	Comparison of fermentation and spoiling processes of grape and fruit wines	DI/GC-FID	Polychroniadou et al. (2003)
<i>Others</i>				
Alcohol-free beer	Selected aroma compounds/3	Studies on aroma changes in alcohol-free beer depending on fermentation conditions	HS/GC-FID	Iersel et al. (1999)
Black tea	Aroma compounds (alcohols, aldehydes, terpenoids)/26	Differentiation of different sorts of tea depending on their origin	SDE/GC-MS	Borse et al. (2002)
Coffee	Selected volatile compounds/8	Classification of different sorts of coffee	Electronic nose, HS-SPME/GC-FID and GC-MS	Freitas et al. (2001)
Coffee	Selected aroma compounds (furanes, nitrogen compounds)/44	Characterization of the product	HS-SPME/GC/GC-MS	Ryan et al. (2004)
Coffee, fruit juice, vegetable oil	Aroma compounds	Characterization of the products	SPME, HS-SPME, HS and LLE/GC-FID and GC-MS	Yang and Peppard (1994)
<i>Eucalyptus</i> honeys	Aroma compounds (benzene derivatives, hydrocarbons, terpenoids)/91	Honey authenticity testing; identification of markers confirming authenticity of honeys	SE/GC-FID and GC-MS	D'Arcy et al. (1997)

Honeys	Aroma compounds (acids, alcohols, aldehydes, furanes, hydrocarbons, ketones, terpenoids)/86	Differentiation of honeys depending on botanical and geographical origin; identification of markers confirming authenticity of honeys	HS-SPME/GC-MS	Soria et al. (2004)
Honeys	Aroma compounds (alcohols, aldehydes, esters, furanes, ketones, terpenoids)/110	Differentiation of honeys depending on botanical and geographical origin; identification of markers confirming authenticity of honeys	DHS/GC-MS	Radovic et al. (2001)
Honeys	Aroma compounds (acids, alcohols, aldehydes)/48	Differentiation of honeys depending on botanical origin; identification of markers confirming authenticity of honeys	SDE/GC-FID and GC-MS	Guyot et al. (1999)
Honeys	Aroma compounds(acids, alcohols, aldehydes, furanes, hydrocarbons, nitrogen compounds, phenols, terpenoids)/72	Honey authenticity testing; identification of markers confirming authenticity of honeys	SDE/GC-FID and GC-MS	Guyot et al. (1998)
Liquor "Cupuassu"	Aroma compounds (alkylpyrazines)/21	Characterization of the product, determination of pyrazine derivatives	HS-SPME/GC-AED and GC-MS	Oliveira et al. (2004)
Mint products (candies, tea, drops, chewing gum)	Menthol and menthone	Determination of menthol and menthone contents	HS-SPME/GC-FID	Ligor and Buszewski (1999)
Mustard paste	Aroma compounds/16	Characterization of different sorts of mustard paste	SDE and HS-SPME/GC-MS	Cai et al. (2001)
Potato crisps	Hexanal	Monitoring of rancidity state	HS-SPME/GC-MS, SE/HPLC-UV and HPLC-MS	Sanchez-Silva et al. (2004)
Potato crisps	Volatile compounds derived from lipid and carbohydrates degradation (acids, alcohols, aldehydes, ketones)/37	Monitoring of aroma changes during storage	HS-SPME/GC-MS	Sanches-Silva et al. (2005)
Soymilk	Selected aroma compounds/3	Monitoring of organoleptic quality of the product	SPE/GC-FID	Wang et al. (1998)
Tea	Aroma compounds (acids, alcohols, aldehydes, esters, nitrogen compounds, terpenoids)/77	Classification of different sorts of tea	SDE/GC-FID and GC-MS	Togari et al. (1995)
Tomato sauce	Volatile components characteristic for products containing raw or processed garlic	Controlling of type and contents of garlic fragrances in sauces	HS and HS-SPME/GC-MS and HS/MS	Dittmann et al. (2000)
Vegetable oils, fruit juices, tomato sauces	Volatile compounds	Classification of the products	Electronic nose	Penza et al. (2001)
Wheat bread	Aroma compounds formed during thermal processing (acids, aldehydes, ketones, nitrogen compounds, sulphur compounds)/51	Identification of key-odorants for toast aroma	SE/pLC/GC-FID, GC-O and GC-MS	Rychlik and Grosch (1996)

Abbreviations: O – olfactometric analysis detector, SDE – simultaneous distillation and solvent extraction, SD – steam-distillation, PTR – proton transfer reaction, MS – mass spectrometry, GC – gas chromatography, SPME – solid phase microextraction, HS – headspace, DHS – dynamic headspace, SPE – solid phase extraction, HPLC - high performance liquid chromatography, SFE – supercritical fluid extraction, SD – steam distillation, TEA – thermal energy analysis, FID – flame ionization detector, LLE – liquid-liquid extraction, LLCE – liquid-liquid continuous extraction, pLC – preparative liquid chromatography, pTLC-preparative thin layer chromatography, pGC – preparative gas chromatography, ECD – electron capture detector, FD – fluorescence detector, DI – direct injection, DAD – photodiode array detector, ME – microextraction, UV – UV detector, FPD - flame photometric detector, AED – atomic emission detector, SBSE – stir bar sorptive extraction, NPD – nitrogen-phosphorus detector, SE – solvent extraction, TD – thermal desorption, RI – refractometric detector.

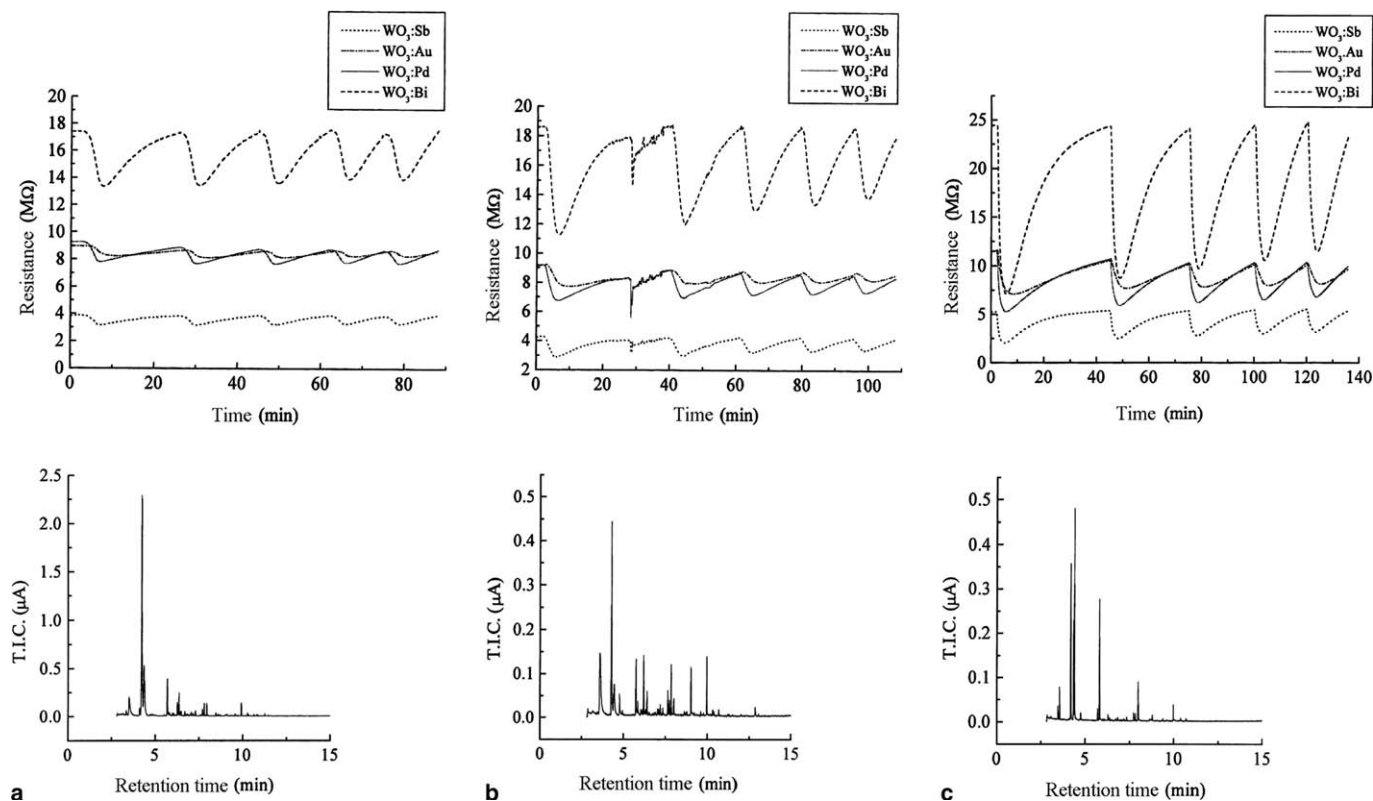


Fig. 3. Typical "aromagrams" of different olive oils by using electronic nose (upper) and GC-MS technique (lower): (a) olive oil "extravirgin", (b) olive oil "sansa", (c) olive oil "Capitanata" (Reproduced from Penza et al., 2001).

action of volatile compounds with the sensor matrix leads to the conversion into an electrical signal. The response of the circuit versus time creates an aromatic profile of the sample's odour. Required information on the product can be extracted from the obtained profile by using proper chemometric methods. The sensors responses can also be correlated with data obtained from organoleptic analysis through connection with an artificial neuron network (Wilkes et al., 2000). In spite of the potentially high sensitivity of sensors, the detection limits achieved in practice usually reach tenths of ppm. This decrease of the sensitivity of the circuit, with respect to the theoretically high sensitivity of sensors, results mainly from limitations of headspace generation techniques (Mielle & Marquis, 1999). The sensitivity of bulk-acoustic wave (BAW) and surface-acoustic wave (SAW) sensors is limited by the noise level at the high operating frequencies of the circuit. In sensor circuits of metal-oxide semiconductor and polymer conductor sensors in turn, a significant drift of the baseline is observed with time and temperature changes (Mielle, 1996). Oxide sensors, commercially available and relatively inexpensive, have low selectivity and like polymer sensors they are susceptible to contamination due to irreversible adsorption of some odour components (such as sulphur compounds and weak acids) on the sensor surface (Mielle, 1996; Wilkes et al., 2000). This can be the cause of devastation of the sensor and require its replacement and renewed calibration of the equipment. The main limitation of the use of "elec-

tronic noses" is their high sensitivity to such matrix components like ethanol, carbon dioxide and water vapour (Mielle, 1996). For this reason, the analysis of alcoholic and carbonated beverages may require an additional stage of removing these components from the sample. In spite of some inconveniences, "electronic noses" are used with great success, mainly for quick classification and differentiation of food products without the need (but also the possibility) of determining the chemical composition of the gaseous phase.

An essential aim for creating aromagrams is the identification of marker substances, indicating the occurrence of quality features sought for in the tested product. At this stage, an excellent tool is provided by chromatographic analysis, which permits the separation and identification of individual aromatic substances. However, if a component or components, which best describe the quality of a product, are known, it is possible to by-pass the time-consuming stage of chromatographic separation and to reduce the duration of the whole analysis considerably through the use of the headspace direct mass spectrometry (Dittmann, Zimmermann, Engelen, Jany, & Nitz, 2000; Fenaille et al., 2003; Lorenzo et al., 2002; Marsili, 1999; Peña, Cárdenas, Gallego, & Valcárcel, 2004; Pérès, Begnaud, & Berdagué, 2002; Pérès, Denoyer, Tournayre, & Berdagué, 2002). This relatively new approach to the analysis of odours leads to an aromatic profile of the whole, undivided into singular components, of the gaseous phase of the product.

A quantitative evaluation of selected fragmentary ions specific for a known marker substance, in connection with chemometric analysis of data, provides the desired results. On this basis, a method of monitoring the amount of garlic aroma in tomato sauces and simultaneous discerning of the type of food additive has been successfully elaborated (Dittmann et al., 2000). On the basis of the mass spectrum of the total ion current, the main odour components responsible for the aroma of garlic (i.e. allyl disulphide, allyl sulphide and methylallyl sulphide) have been identified, as well as four fragmentation ions (m/z 73, 81, 114, 120) present in the mass spectra of these compounds, as markers subsequently determined by a static headspace method in connection with mass spectrometry (HS/MS). The Authors pointed out the speed, simplicity and lower cost of the new method in comparison with chromatographic analysis. Direct headspace analysis using mass spectrometry techniques is called by some authors a sort of the electronic nose, as each fragmentary ion present in the total mass spectrum of the gas phase of the product can be treated analogously as one sensor of a typical electronic nose. Thus, the amount of obtained data is greater because the observed number of fragmentary ions during full scanning in a broad mass spectrum (several hundred) is greater than the typical number of sensors (several). In addition, there is a possibility of adjusting the selectivity and sensitivity of the method through a change of scanning parameters from full to a single ion monitoring (Dittmann et al., 2000). A basic deficiency of this technique is – similarly as an electronic nose – lack of possible identification and quantitative determination of individual compounds.

3.2. Chromatographic techniques

A detailed qualitative and quantitative analysis of aromatic components of food is facilitated by the use of chromatographic techniques. For obvious reasons, gas chromatography with various detection methods has found greatest application in the determination of volatile aromatic substances. Most often the flame ionisation detector (FID) is used, which as an universal detector allows to obtain a full aromagram of a given product. In order to obtain the aroma profile connected with a selected class of compounds e.g. sulphur compounds such as alkyl sulphides and thiols (Hill & Smith, 2000; Mestres, Busto, & Guasch, 1998) and nitrogen compounds such as alkyl pyrazines in fermented products (Sala, Mestres, Marti, Busto, & Guasch, 2000; Sala, Mestres, Marti, Busto, & Guasch, 2002), it is also possible to use selective detectors. Determination of mentioned selected classes of compounds can be a good indicator of the quality, as the influence of these fermentation side-products on the bouquet is negative and very strong. An excellent solution is the application of gas chromatography along with a mass spectrometer, because it permits simultaneous identification of aromatic components of a food product. The possibility of sensoric analysis and semi-quantitative evaluation of components,

which really influence the aroma among all the volatile compounds present in a sample, i.e. components sensorically active, is provided by the olfactometric detector, which allows direct olfactory evaluation of substances eluted from a column (Boudhrioua et al., 2003; Farkaš et al., 1997; Ferrari et al., 2004; Ferreira, Aznar, López, & Cacho, 2001; Ferreira, Ortin, Escudero, López, & Cacho, 2002; Frank, Owen, & Patterson, 2004; Ruth, Roozen, Cozijnsen, & Posthumus, 1995; Rychlik & Grosch, 1996; Triqui & Bouchriti, 2003). Quantitative olfactometric methods can be divided into two groups: methods which evaluate the intensity of odour of analytes as a function of time during a single chromatographic analysis (e.g. OSME) and methods based on thresholds of sensoric perceptibility, where the analysis of a series of dilutions of an odour extract is conducted, until reaching the moment when no more odour is detectable in the eluent from the column (e.g. CHARM, AEDA) (Mariaca & Bosset, 1997; Pollien et al., 1997). Most often an olfactometric detector is employed together with other detectors (FID, MS) which permits the identification and exact analysis of components essential for the odour of a product.

In contrast with gas chromatography, liquid chromatography is rarely used in odour analysis, chiefly as a preparative column chromatography as a stage in the preparation of a sample before the chromatographic analysis itself (Bhattacharjee, Singhal, Gholap, Variyar, & Bongirwar, 2003; Ferreira et al., 2002; Guth, 1997; Ledauphin et al., 2004; Mallouchos et al., 2003a, Mallouchos, Komaitis, Koutinas, & Kanellaki, 2003b; Rychlik & Grosch, 1996; Webster et al., 2000). Another application of liquid chromatography is the determination of thermally unstable compounds such as amines or aldehydes or compounds relatively sparingly volatile. However, this is usually connected with the necessity of converting determined substances into derivatives permitting detection with the use of detectors popular in liquid chromatography, such as a fluorescent detector (FD) or a photodiode array detector (DAD) which complicates the analysis (Wilkes et al., 2000).

4. Preparation of samples in the determination of volatile aromatic compounds

The determination of aromatic substances by instrumental techniques consists of two stages. The first phase of the analysis is particularly important, the isolation of analytes from the complicated matrix presented by most food products. The aspect of “aromagrams” and the possibility of their multiple use for the evaluation of food quality closely depends on the isolation procedure. The isolated product must be possibly representative, therefore the choice of an appropriate sample preparation method becomes crucial. Depending on the properties of the food product, many isolation techniques are in use. Direct chromatographic analysis can be applied rarely, in the case of simpler matrices such as alcoholic beverages or more

intensive aromas (Apostolopoulou et al., 2005; Bardi et al., 1997; Clemente-Jimenez, Mingorance-Cazorla, Martinez-Rodriguez, Heras-Vázquez, & Rodriguez-Vico, 2004; Cortés et al., 2005; Ferrari et al., 2004; Hernández-Gómez et al., 2003; Hernández-Gómez et al., 2005; Madrera, Gomis, & Alonso, 2003a; Madrera et al., 2003b; Polychroniadou et al., 2003, Porto, Pizzale, Bravin, & Conte, 2003; Silva, Malcata, & Revel, 1996; Soufleros, Mygdalia, & Natskoulis, 2004; Torrea et al., 2003). In most cases it is essential to isolate the desired food product components in order to eliminate interfering signals coming from the complex matrix or for enrichment. Volatile aromatic substances are usually characterized by low odour thresholds and they affect the organoleptic quality already at very low concentrations. Among the solutions presented in literature we most often find the following: solid phase microextraction (SPME), headspace analysis techniques (static – HS and dynamic – DHS) and distillation with water vapour (SD). Some application is also found by supercritical fluid extraction (SFE) and solid phase extraction (SPE), but because of the lower quality of results and great labour and time consumption, less use is made of the classic liquid–liquid extraction (LLE) or in the case of extraction from solid products – solvent extraction (SE).

4.1. Solvent extraction techniques

The basic deficiency of the classical extraction by solvent, after which usually concentration of the extract through distilling off part or all of the solvent occurs, is not only the extension of the analysis in time – which is connected with the need to go through many stages of sample preparation, and this leads to loss of analytes in each of subsequent stages – but also low selectivity of isolation. The use of typical organic solvents usually leads to coextraction of other components of the matrix apart from the desired volatile fraction of the product, which decreases the delectability of trace analytes (Sides, Robards, & Helliwell, 2000). Another essential deficiency is the necessity of using high-purity solvents in order to avoid the creation of so-called background coming from trace impurities in the solvent, which are concentrated in the extract during its enrichment. The problem of extractant purity is related to all solvent techniques, also distillation with water vapour or extraction to the solid state. High consumption of high-purity solvents raises the cost of analyses. In spite of many deficiencies, extraction by solvent still remains a satisfying solution and provides good results, especially with simple matrices such as fruit and vegetables, juices and alcoholic drinks. A great advantage of extraction by solvent in comparison with headspace analysis techniques and solid phase microextraction, is the possibility of using a greater amount of the sample and, in consequence, better enrichment of analytes after the removal of the solvent and to obtain higher sensitivity of the method. For example, the extraction of aromatic substances from a sardine by methylene chloride (Triqui & Bouchriti, 2003) and subsequent

vacuum distillation, permitted the determination of almost twice as many aromatically active compounds than solid phase microextraction which was likely caused by the use of six times more material extracted by the solvent.

In products such as wines, we find examples of employing continuous liquid–liquid extraction (LLCE) (Baptista, Tavares, & Carvalho, 2001; Castro, Natera, Benitez, & Barosso, 2004; Maicas et al., 1999; Rocha et al., 2000; Valero et al., 2002). From a comparison made between solid phase microextraction (SPME) and LLCE (Castro et al., 2004) and their use to the extraction of volatile compounds from wine, the result is that both techniques generally achieve comparable limits of detection and determination, as well as linearity ranges for proper quantitative determination of analytes of this type. At similar repeatability of measurements (<14%), LLCE shows, however, lower sensitivity with respect to some components of the bouquet, which is connected to lower extraction efficiency. Besides, LLCE, as any other extraction by solvent, causes a solvent peak in the chromatogram, which, depending on its area, may prevent the determination of more volatile analytes such as ethyl acetate. The application of solventless extraction techniques such as SPME eliminates this problem.

4.2. Steam distillation techniques

Extraction by solvent in connection to concentration of the extract through the vacuum distillation technique or under nitrogen is one of the oldest techniques used in the analysis of odours. Another technique known for a long time for the isolation of aromatic substances from a wide range of matrices is steam distillation (SD). When used in the analysis of such products as fish (Zhu, Aviles, Conte, Miller, & Perschbacher, 1999), cured meat products (Sen, Seaman, & Page, 1997), dairy products (Ulberth & Roubicck, 1995), wines (Ferreira et al., 1995), it is usually used for the initial extraction of volatile substances, after which the extract is analysed with a selected headspace analysis technique. Such an approach is especially founded in the case of matrices containing components which make direct headspace analysis difficult by bonding volatile compounds in its structure or causing an unfavourably high partition coefficient of analytes between the sample and the gas phase. Because of the use of elevated temperature, SD can lead to thermal degradation of odour components and create artefacts. This lowers its applicability in the analysis of products containing thermally unstable substances and vulnerable to oxidation. Substantial dilution with water of the obtained extract is also undesired. This problem can be overcome by using simultaneous distillation and solvent extraction (SDE), but it requires the use of complicated instrumentation. This technique has been employed in the analysis of such products as: meat (Dirinck, Opstaele, & Vandendriessche, 1997; Farkaš et al., 1997), vegetables (Kocsis, Amtmann, Mednyánszky, & Korány, 2002), cheese (Dirinck & Winne, 1999), tea (Borse

et al., 2002; Togari et al., 1995), honey (Guyot et al., 1999), mustard (Cai, Liu, & Su, 2001). The application of SDE to the analysis of the volatile odour fraction of mustard (Cai et al., 2001) allowed the extraction of a broader range of analytes, including high-molecular-weight and difficultly fugacious compounds such as higher fatty acids, than in the result of SPME. In comparison with the second, a lower sensitivity to vestigial analytes was obtained. The authors admitted also the superiority of SDE in the quantitative evaluation of the analysed compounds because of the somewhat better repeatability of results calculated as relative standard deviation in relation to SPME. Moreover, a relatively low productivity of extraction has been found for most volatile analytes, because of losses and the creation of artefacts due to such conversions as hydrolysis and pyrolysis of sample constituents. Another cause of artefacts is found in oxidation processes of odour components, facilitated by the high temperature of the process (Sides et al., 2000). The apparatus of Lickens-Nickerson, mostly used in these processes, eliminates these effects only in part by lowering the boiling temperature of the sample by reducing the pressure.

Because of the low selectivity of solvent extraction or steam distillation in relation to odour substances, sometimes additional purification of the extract is practised, e.g. using solid phase extraction (SPE). The SPE technique becomes handy in the isolation of medium-volatile odorous compounds. Most often, ion-exchange beds are in use for the extraction of substances having acidic character, such as organic acids (Diéguez, Díaz, Peña, & Gómez, 2002; Nascimento, Cardoso, Keukeleire, Lima-Neto, & Franco, 2000; Park et al., 1999) and phenols (Ng, Lafontaine, & Harnois, 2000) which are difficult to extract reproducibly and efficiently using other techniques, because of the high polarity and high partition coefficient between sample and gaseous phase in relation to other odour components.

4.3. Supercritical fluid extraction

A relatively new and unexploited to a satisfying degree is supercritical fluid extraction. In comparison with other solvent techniques it gives a cleaner extract, which also extends the lifetime of a column (Sides et al., 2000). An additional advantage, particularly in comparison with headspace analysis techniques, is the possibility of isolating compounds not easily volatile or strongly bound with the matrix. The scarce use of this technique in the analysis of odours heretofore (Bhattacharjee et al., 2003) probably results from the difficulty in obtaining an efficient extraction of polar analytes by carbon dioxide. Perhaps better results will be obtained using water in supercritical state as the extractant.

4.4. Headspace analysis techniques

In the course of the last years the instrumental odour analysis has been dominated by a group of headspace anal-

ysis techniques. In general, headspace analysis exemplifies rather the liberation of volatile components from the matrix than permits the determination of the total content of these components, therefore it can be more easily correlated with the results of sensoric analysis.

4.4.1. Static headspace analysis technique

The simplest and relatively cheap technique from this group is static analysis (HS). In comparison with classic solvent extraction and dynamic analysis, equilibrium HS in fact reduces the time needed for the preparation of a sample, also by providing the possibility of automating the whole procedure (Wilkes et al., 2000). Besides – the extracts obtained are considerably cleaner and they do not contain undesirable components transferring to extracts obtained by extraction techniques with solvents, such as liquid–liquid extraction, distillation with water vapour or simultaneous distillation and solvent extraction. HS is a conservative technique – it does not damage the sample or the odour components and does not create artefacts. On the other hand, the headspace analysis techniques show a tendency to discriminate less volatile compounds, therefore in quantitative analysis the need arises to produce calibration curves separately for each analyte (Wilkes et al., 2000). In the case of rich aromagrams, the time gained in the preparation of the sample can be lost for calibration.

The main disadvantage of static HS is the lack of enrichment of analytes, which sometimes leads to insufficient sensitivity to vestigial components of the extract. A comparison of the HS technique and the headspace solid phase microextraction (HS-SPME) in the analysis of beer bouquet (Jeleń, Wlazły, Wąsowicz, & Kamiński, 1998) has shown the high linearity of both methods in the range of concentrations tested, however, the determination limits obtained by the HS-SPME technique were 2–5 times lower than those obtained by the HS technique, with respect to most analytes. The higher repeatability of the method using HS (relative standard deviation for 9 of the 11 determined compounds below 4%, while for HS-SPME only for 5 out of 11 compounds) resulted probably from the way of conducting the determination – HS – automatically, HS-SPME – manually. Because of the reduced possibilities of determining trace analytes in comparison with other similar techniques, headspace analysis in static conditions finds its application above all as a method for generating the gaseous phase analysed subsequently by the electronic nose technique (Berna, Lammertyn, Saevels, Natale, & Nicolai, 2004; Biswas, Heindselmen, Wohltjen, & Staff, 2004; Freitas et al., 2001; Guadarrama, Fernández, Íñiguez, Souto, & Saja, 2000; Martin, Oliveros, Pavón, Pinto, & Cordero, 2001; Martin, Pavón, Cordero, & Pinto, 1999; Oliveros et al., 2002; Oshita et al., 2000; Penza & Cassano, 2004a, 2004b; Santos et al., 2004; Shaw et al., 2000; Steine et al., 2001) or by the direct mass spectrometry method.

4.4.2. Dynamic headspace analysis technique

The relatively low sensitivity of static headspace analysis results from the fact that a state of equilibrium is reached between the gaseous phase and the sample. This problem is eliminated by the dynamic headspace analysis (DHS), called also the 'purge and trap' technique (PT) – a technique of elution with simultaneous capture of analytes, in which enrichment occurs in the result of continuous shift of the state of equilibrium between concentrations of analytes in the matrix and in the headspace phase. In this way the detection threshold is lowered from the ppm level (HS) to the ppb level (DHS) (Supelco Bulletin 923, 1998). Dynamic headspace analysis is a general conception; in its range there are many capture methods as well as methods of desorption of analytes from the trap. Each of the methods has its advantages and deficiencies. Cryogenic traps are exceptionally sensitive to water, therefore in order to avoid their choking, water vapour should be very effectively removed from the gas before reaching the trap. Capturing analytes by cooling is most effective with regard to most volatile compounds (Pillonel, Bosset, & Tabacchi, 2002). Moreover, such inconvenient effects as degradation of analytes and creation of artefacts, irreversible bonding of substances and overloading of the trap do not take place in cooling. A deficiency of this solution is, however, the relatively high cost of equipment and the relatively long time of desorption and renewed cooling before the next analysis (Pillonel et al., 2002). The application of popular traps based on solid adsorbents such as porous polymers – Tenax, Porapak, Chromosorb or activated carbon is also facing many difficulties such as low capacity of some adsorbents with respect to very volatile constituents, and in consequence overloading of the trap and loss of analytes, creation of artefacts due to catalytic action of the bed, favouring and irreversible adsorption of long-chain or polar compounds (Pillonel et al., 2002). Solid adsorbents can have an alternative in the form of non-polar liquid sorbing agents, e.g. silicone polymers, as they do not create competition and discrimination of short-chain compounds in relation to compounds with greater molecular mass and they do not show any catalytic action. Liberation of captured analytes occurs mostly due to thermal desorption. This is a very effective method (ensuring 100% desorption of analytes), but at the elevated temperature of processes, decomposition of labile components may occur. In comparison with an alternative solvent desorption, thermal desorption shows no solvent peak in the chromatogram which may obscure more volatile compounds, does not introduce contaminations to the extract coming from the solvent and it does not cause losses of analytes (Sides et al., 2000). Furthermore, desorption by solvent provides difficulties when it comes to automation of the process. On the other hand, it is conducted in more mild conditions, which is an advantage. It is worth noting, that the use of thermal desorption is not confined to dynamic headspace analysis.

Direct thermal desorption of analytes from a sample placed in a special apparatus is also being used. In spite of the established sensitivity several score times higher in this technique in comparison with the solid phase microextraction, its application is limited to samples with low water content and containing no thermally labile components (Pillonel et al., 2002). Irrespective of methods of realization of the capture and desorption stages of analytes, the dynamic headspace analysis is characterized by its longer extraction time in comparison with other solventless techniques – several or even less than 20 times longer than for the solid phase microextraction (Song, Gardner, Holland, & Beaudry, 1997; Supelco Bulletin 923, 1998). Another shortcoming is the sensitivity to water in the system. In principle, all traps, particularly in the case of samples of high humidity, capture some amount of water which disturbs the analysis and can even lead to damage of the equipment. For this reason it is indispensable to apply some additional measures aiming at removal of water, such as: drying of the bed with gas, condensation of water vapour ahead of the trap, separation by membrane (Pillonel et al., 2002). The removal of water is unfortunately one of the reasons of losses in volatile and polar analytes often taking place. In spite of numerous methodological difficulties connected with headspace analysis in dynamic conditions, many publications have appeared so far on the optimisation of this technique in the analysis of the odour of meat and fish products (Dirinck et al., 1997; Hierro, Hoz, & Ordóñez, 2004; Nakai et al., 1999; Refsgaard, Haahr, & Jensen, 1999), fruit and vegetables (Argenta, Mattheis, Fan, & Finger, 2004; Grison-Pigé, Hossaert-McKey, Greeff, & Bessière, 2002; Lavilla, Recasens, Lopez, & Puy, 2002; Lyew et al., 2001; Ruth et al., 1995; Song et al., 1997), cheese and other dairy products (Bellesia et al., 2003; Bintsis & Robinson, 2004; Pérès et al., 2002; Contarini & Povolo, 2002; Thierry, Maillard, Hervé, Richoux, & Lortal, 2003; Thierry et al., 2004), vegetable oil (Kanavouras, Kiritsakis, & Hernandez, 2005) and honey (Radovic et al., 2001). Chromatographic analysis of the aroma of various kinds of smoked ham, using an adsorption Tenax TA trap and thermal desorption (Dirinck et al., 1997) and with the use of simultaneous distillation and extraction by solvent (SDE), has shown the lower repeatability of the first method, what has been linked by the Authors foremost with equipment deficiencies such as choking of the trap and leaks in the system, but also with high content of fat and inhomogeneity of products of that type. The high fat content was probably also the cause of the appearance of peaks in aromagrams coming from air contamination, which very easily sorb on the surface of fatty samples, which has been observed earlier by other authors. Because of the high standard deviations obtained when using the DHD technique, the authors acknowledged the method using SDE as being more trustworthy in quantitative determination. The more, in the result of SDE a greater number of compounds has been isolated, which resulted in a rich array of chromatograms. The experiment-

ers pointed out, however, the possibility of creating decay products of labile compounds in the conditions of extraction, in particular of sulphur compounds.

4.5. Solid phase microextraction technique

Particular attention should be given to the instrumental analysis of organoleptic quality and the technique of solid phase microextraction (SPME), developed by Pawliszyn and co-workers in 1990 (Kataoka, Lord, & Pawliszyn, 2000; Pawliszyn, 1997). In the determination of volatile odour substances the version realized in the headspace phase (HS-SPME) is particularly useful. The SPME technique requires only a small amount of sample and permits to isolate and enrich volatile and half-volatile analytes from matrices both in the solid and liquid states in short time, in a simple way and with relatively low financial outlay. It ensures the linearity of results in a broad range of concentrations (up to ppt) (Supelco Bulletin 869 A, 1998). It is a conservative technique – allowing the preservation of the natural contents and composition of the sample – it does not require the use of high temperatures and pressures, nor solvents or complicated equipment. Manipulation of the sample and the possibility of loss of analytes is insignificant, some difficulty may be found in the isolation of less-volatile compounds or with high affinity to the matrix, e.g. isolation of polar compounds such as organic acids from matrices of polar character, like beverages. In such cases derivatisation is used or the extraction conditions are optimised in another way (e.g. temperature, duration of the exposition of the fibre, the type of fibre, ionic strength of the matrix) in order to increase recovery and sensitivity. An example of an approach using derivatisation can be testing the influence of carbonyl compounds – aldehydes and ketones – on the organoleptic properties of alcoholic beverages depending on their type and the degree of their condensation, using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) as the reagent converting carbonyl compounds into oxime derivatives and subsequent solid phase microextraction and gas chromatography with electron capture detection (ECD) (Wardencki, Sowiński, & Curyło, 2003). Although SPME preceded by derivatisation using various agents is commonly used in simple or environmental samples, there are not yet many examples of exploitation of this approach in food matrices. Anyhow, the most useful version seems to be on-fibre derivatisation. Except methods designed for alcoholic matrices mentioned above, there are reported also in the literature applications of derivatisation in lipid matrices such as vegetable oils (Stashenko et al., 2000). In this case pentafluorophenylhydrazine (PFPH) was used as a derivative.

4.5.1. Advantage of SPME over other sample preparation techniques

The numerous comparisons the SPME technique with other extraction techniques of odorous compounds present in literature, often show the superiority of the former tech-

nique. The essential advantage of SPME, common for techniques using headspace extraction, is the possibility to isolate and enrich odorous components without interference from the remaining matrix components. In contrast with extraction techniques based on total extraction of analytes from the matrix, SPME is based on an equilibrium of analyte concentrations in the sample, in sample headspace and in the stationary phase of the fibre. Therefore, in spite of the fact that optimal extraction time is the time needed to achieve a state of equilibrium, it is possible to shorten the time of extraction in a reproducible way under the condition that stability of conditions is preserved (Vallejo-Cordoba, González-Córdova, & Estrada-Montoya, 2004). Similarly as static headspace analysis (HS), HS-SPME shows a tendency to discriminate less-volatile compounds, but adsorption of analytes on the fibre causes their enrichment and an essential increase of the sensitivity of the technique. While HS permits the determination of odorous components at the ppm level (Supelco Bulletin 923, 1998), the SPME technique allows to achieve two orders lower detection limits. In comparison with HS, lower sensitivity and productivity of extraction for extremely volatile compounds has been observed (Doleschall et al., 2001; Yang & Peppard, 1994). When comparing this pair of techniques it should be noted that HS-SPME prevents the introduction of water to the chromatographic column and in consequence its premature destruction (Yang & Peppard, 1994). Solid phase microextraction has also advantages over dynamic headspace analysis (DHS) – it preserves the mild conditions of the process, which cause no changes in the composition of the sample (e.g. due to thermal decomposition) and cause no creation of artefacts (e.g. due to thermal degradation of the bed material in the trap) (Marsili, 1999), and also shows greater repeatability of results. The average precision obtained with the SPME technique, calculated as relative standard deviation, lies in the range <1–12%, while using the DHS technique usually a precision of 1–30% is achieved (Supelco Bulletin 923, 1998). Besides, in the case of SPME the remains of analytes from preceding analyses are not introduced into the column, which occurs in headspace analysis in dynamic conditions (Wilkes et al., 2000). Both techniques could be utilized together with gas chromatography in order to distinguish milk in dependence on the thermal processing method (Contarini & Povolito, 2002).

A better recovery of greater molecular weight compounds (2-heptanone, 2-nonanone, 2-undecanone) has been noted when using the HS-SPME technique, while the DHS technique gave higher extraction yield for compounds with small molecular weight (acetone, 2-butanone), preserving a comparable repeatability of results using both techniques. Similar results have been observed when comparing extraction yields of volatile aldehydes with HS-SPME and static headspace analysis (HS) techniques from vegetable oils (Doleschall et al., 2001). A comparison of results of analysis of volatile butter fraction (Povolito & Contarini, 2003) has shown a more efficient extraction of

fatty acids of relatively low volatility using the HS-SPME technique than the DHS technique. The better extraction of medium-volatile compounds, compounds of low volatility and such of higher molecular weight using the SPME technique in comparison with headspace analysis techniques is not a rule. In the result of comparing the bouquets of Parmesan cheese isolated with the use of the HS-SPME and DHS techniques and determined chromatographically (GC) it has been established that less-volatile components were extracted more efficiently by the DHS technique (Bellesia et al., 2003). Generally it can be stated that the total productivity of solid phase microextraction in comparison with the 'purge and trap' technique is usually lower. It has a relationship above all with the much greater sorbing area of the trap than that of fibre and also with the smaller amount of sample extracted with the SPME technique (Povolo & Contarini, 2003). Aromagrams obtained using SPME are more readable but usually more modest because of the number and concentration of isolated compounds (Fig. 4).

4.5.2. Disadvantages of SPME technique

The sensitivity of headspace analysis techniques, including also SPME, strongly depends upon the composition of the matrix and is highly susceptible to changes in its composition, for example to changes in the fat content in the product. High fat content reduces the extraction productivity, foremost in relation to less volatile components, therefore for products considerably differing in fat contents (e.g. whole milk and skim-milk), in order to perform a quantitative evaluation, separate calibration curves should be determined for each variant (Wilkes et al., 2000). The sensitivity of SPME from edible oil samples is lower for the same analytes in comparison with water samples, because the solubility of odorous components in oil is much higher than in water. Thus the analysis of the odour of oils requires usually a higher extraction temperature (Yang & Peppard, 1994). In a similar way the presence of organic solvents such as ethanol reduces the adsorption of analytes on fibre. The results obtained using the SPME technique depend strongly not only on the composition of the matrix but also on process conditions, which may complicate the quantitative determination (Sides et al., 2000). Each change of extraction parameters having an effect upon the division ratio and speed of adsorption will have an influence on the productivity and repeatability of the extraction. Because of the susceptibility to the composition of the matrix and conditions of carrying out the isolation, methods of extrinsic calibration should not be used in the case of complicated matrices – solid, non-homogeneous, with differentiated quantitative and qualitative content, or containing substantial amounts of organic solvents, proteins, fats (Supelco Bulletin 929, 2001). In such cases it is advisable to apply an external standard methods, most favourably – isotope dilution analysis, but solid samples require then homogenisation in liquid phase. It has been established that in the case of simple matrices such as alcoholic

beverages from oranges (Porto et al., 2003), when there is no need to enrich the analytes, a better solution may be provided by direct injection the sample to a gas chromatograph, which gives more reliable quantitative results. An additional argument against the use of SPME in the case discussed by the authors is the low productivity of extraction of polar analytes such as low and medium molecular weight alcohols (methanol, isobutanol, *n*-butanol, isoamyl alcohols), even in comparison with direct analysis without enrichment. The presence in the sample of large amounts of analyte with a high partition coefficient stationary phase of fibre – gaseous phase causes the appearance of the competition effect and displacement of analytes from the surface of the fibre. A reduction of the extraction time in such a situation lowers the probability of overloading the fibre and subsequent false results (Roberts, Pollien, & Milo, 2000). In samples of alcoholic beverages with high ethanol content, the extraction productivity falls with the increase in concentration of ethyl alcohol, therefore usually dilution of the sample to an ethanol content of 10–20% is in use. The effect of competition is of great importance in SPME realized by direct immersion of the fibre in a liquid matrix. A greater reduction in sensitivity has been observed with an increase of ethyl alcohol concentration in relation to terpenoids isolated from wine in comparison with HS-SPME (Garcia et al., 1998).

In the case of simple matrices such as Tequila which contain no components such as fats or proteins which might interfere with and render the extraction difficult, and which contain medium- and difficultly volatile odorous components (such as long-chain esters of fatty acids), SPME is preferred realized through direct immersion of fibre in the matrix (Vallejo-Cordoba et al., 2004). It allows not only to obtain a reduced extraction time, but also increases its productivity and substantially lowers the detection thresholds of these analytes, as the productivity for medium- and difficultly volatile compounds is higher and possible at all, and for easily volatile it comes close to that of HS-SPME. Rinsing the fibre after extraction in order to remove interfering substances extends the possibilities of using this version of SPME. Rinsing with warm distilled water in order to remove saccharides extracted together with the determined analytes has been used during the isolation of components of the bouquet of whisky, using a homologous SBSE technique (*Stir Bar Sorptive Extraction*) (Demyttenaere, Sánchez Martínez, Verhé, Sandra, & Kimpe, 2003).

4.5.3. Importance of appropriate selection of fibre

In spite of some deficiencies of the technique of the solid phase microextraction, it seems to be ideal for purposes connected with the determination of odorous compounds. An even broader range of commercially available fibres allows to determine a broader range of analytes. An appropriately selected fibre allows a more selective extraction than using headspace analysis techniques, both static and dynamic, e.g. volatile polar fatty

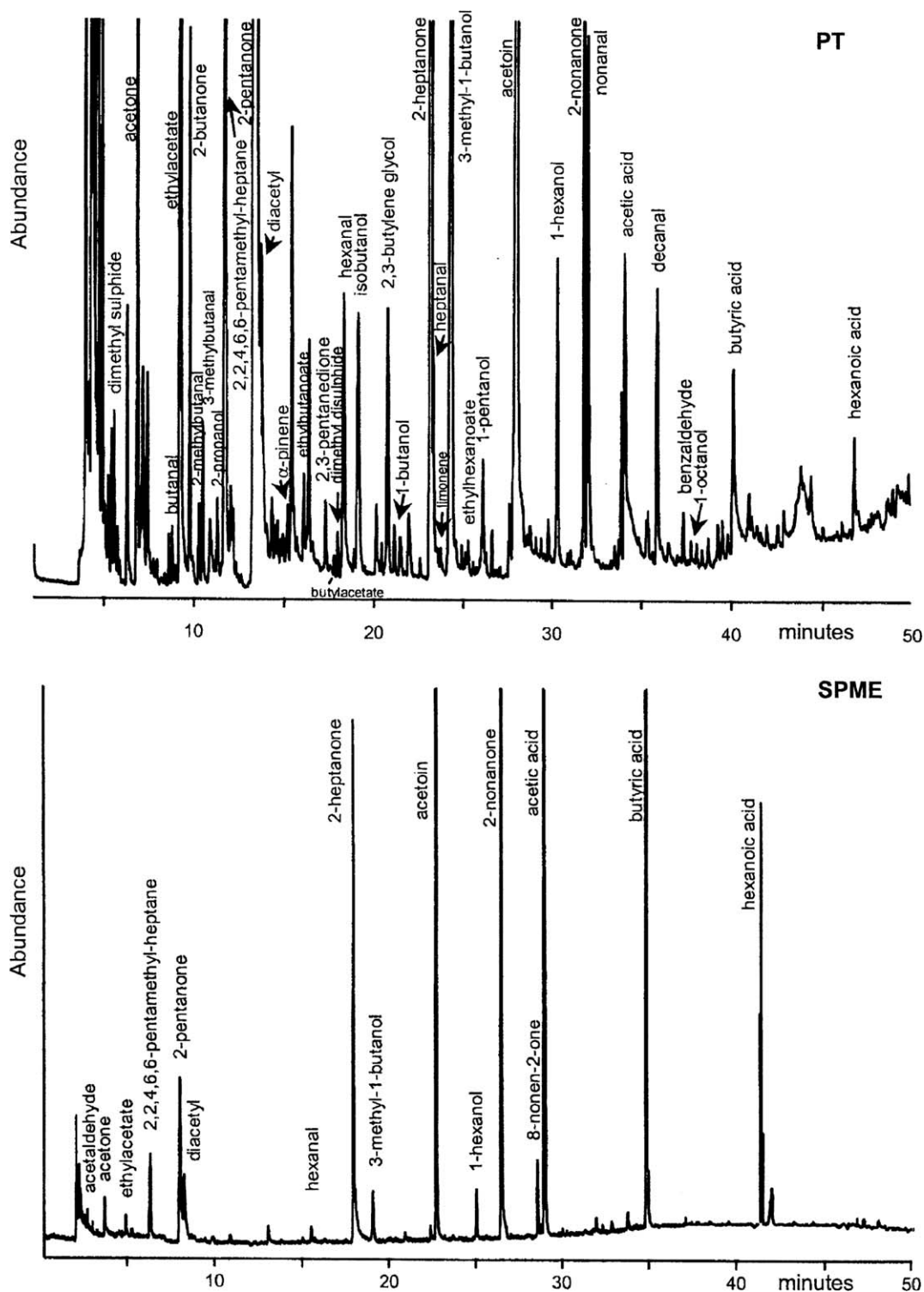


Fig. 4. Profiles for volatile fraction of butter by using GC–MS and: dynamic headspace technique (DHS) (upper) or solid phase microextraction (SPME) (lower) (Reproduced from Povolo and Contarini, 2003).

acids appearing in low concentrations (Marsili, 1999). The choice of the fibre is very important in the analysis of odorous compounds not only because of the composition of the extract obtained, but also because different fibres ensure different repeatabilities of the method in a given case. For example: the aroma of alcoholic beverages from

oranges has been analysed and among four tested fibres (of the type: PDMS – polydimethylsiloxane as the stationary phase, PDMS/DVB – polydimethylsiloxane/divinylbenzene, CAR/PDMS – carboxen/polydimethylsiloxane, DVB/CAR/PDMS) it has been shown that the use of a fibre of the type DVB/CAR/PDMS resulted in relative

standard deviations several times smaller for the determined compounds than the remaining ones (Porto et al., 2003). Among fibres of the PDMS, PA (polyacrylate), PDMS/DVB, CW/DVB (carbowax/divinylbenzene) types exploited for the extraction of fatty acids ethyl esters from the Tequila bouquet – the first turned out to be the best because of its lowest coefficient of variation (CV), below 10% (Vallejo-Cordoba et al., 2004). The suitability of fibres of a given type depends also upon the method of extraction – from the headspace or as the result of direct immersion. In the case of odorous components from wine, the PDMS type of fibre has proved to be optimal for HS-SPME because of the enrichment factor and repeatability, whereas for direct immersion better results were achieved with DVB/CAR/PDMS fibres (Demyttenaere et al., 2003).

4.5.4. Modifications of SPME technique

Depending on the kind of sample, numerous modifications of SPME have been developed in order to broaden the application of this technique. For example, for solid state products such as cured meat products (ham, liver sausage) in which direct immersion of the fibre in the matrix is not possible, a method facilitating the insertion of fibre to the interior of a solid sample has been developed (Ruiz, Ventanas, & Cava, 2001). The method permits the extraction from practically intact material, without excessive manipulation of the sample, thanks to the placement of the needle with the fibre inside an appropriately built perforated tube with a sharpened end, which facilitates driving the whole device into the matrix. In effect, an approximately similar number of extracted compounds has been isolated in comparison with HS-SPME, but the presence of impurity traces on the chromatogram, coming from volatile solvents in air, could be avoided. A deficiency was the somewhat lower repeatability for less volatile components, as well as lack of possibility of using an internal reference in quantitative determinations. In another paper on this method it has been also indicated that lack of homogenisation of the sample can have an effect on the kind and number of isolated components (Andrés et al., 2002).

As mentioned earlier, a small amount of stationary phase deposited on the fibre can lead to low recovery of analytes. For this reason, new modifications of the classic SPME in the form of the SBSE technique (*Stir Bar Sorptive Extraction*) and HSSE (*Headspace Sorptive Extraction*) are under development, permitting the determination of analytes appearing in trace and ultra-trace quantities, even below ppt, which results from a greater amount of stationary phase deposited on a bar thicker than the fibre (Baltussen, Sandra, David, & Cramers, 1999; Bicchi, Cordero, Iori, & Rubiolo, 2000; Demyttenaere et al., 2003). The adsorbed analytes are subsequently undergoing thermal desorption, which requires that the chromatographic system is fitted with equipment for thermal desorption. Advantages of the new techniques include also: slower degradation of the stationary phase and resulting loss of

repeatability and in consequence rare necessity to exchange and calibrate anew (Pillonel et al., 2002).

5. Summary

The examples cited in the paper show the great possibilities in using the determination of volatile compounds for the appreciation of contents of expected and desired food elements, but also for the detection and determination of the level of undesired substances, including not only those which lower the organoleptic quality but often also hazardous to the health of the consumer. At the same time, because of the variety and complicated composition of matrices found in food products and the kind of information we want to obtain on a product, particular importance is gained by the choice of the proper analytic method. The more common use of instrumental analysis in the creation of “aromagrams” in the evaluation of organoleptic quality and safety of food results from limitations characteristic for sensoric analysis. For reasons of objectivity, higher repeatability and reproducibility of results and the possibility of identifying odour and their quantitative estimation, instrumental analysis constitutes not only an excellent supplement to sensoric analysis, but it becomes an indispensable tool in the complete analysis of sensoric quality of food. Besides, the analysis of “aromagrams” provides additional information on the health quality of a product.

The basic advantage of creating aromatic profiles of food products may be the possibility of creating “aromagram” bases on grounds of analyses of a kind of reference products, classified by type, origin or quality. The evaluation of quality on the basis of comparison of the odour profile of a given product with model profiles can constitute an essential supplement and extension of sensoric analysis.

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References

- Andrés, A. I., Cava, R., & Ruiz, J. (2002). Monitoring volatile compounds during dry-cured ham ripening by solid-phase microextraction coupled to a new direct-extraction device. *Journal of Chromatography A*, 963, 83–88.
- Andrés, A. I., Cava, R., Ventanas, J., Muriel, E., & Ruiz, J. (2004). Lipid oxidative changes throughout the ripening of dry-cured Iberian hams with different salt contents and processing conditions. *Food Chemistry*, 84, 375–381.
- Apostolopoulou, A. A., Flouros, A. I., Demertzis, P. G., & Akrida-Demertzi, K. (2005). Differences in concentration of principal volatile constituents in traditional Greek distillates. *Food Control*, 16, 157–164.
- Argenta, L. C., Mattheis, J. P., Fan, X., & Finger, F. L. (2004). Production of volatile compounds by Fuji apples following exposure to high CO₂ or low O₂. *Journal of Agricultural and Food Chemistry*, 52, 5957–5963.

- Arnault, I., Mondy, N., Cadoux, F., & Auger, J. (2000). Possible interest of various sample transfer techniques for fast gas chromatography-mass spectrometric analysis of true onion volatiles. *Journal of Chromatography A*, 896, 117–124.
- Augusto, F., Valente, A. L. P., Tada, E. S., & Rivellino, S. R. (2000). Screening of Brazilian fruit aromas using solid-phase microextraction-gas chromatography-mass spectrometry. *Journal of Chromatography A*, 873, 117–127.
- Baltussen, E., Sandra, P., David, F., & Cramers, C. (1999). Stir bar sorptive extraction SBSE, a novel extraction technique for aqueous samples: theory and principles. *Journal of Microcolumn Separations*, 11, 737–747.
- Baptista, J. A. B., Tavares, J. F. P., & Carvalho, R. C. B. (2001). Comparison of polyphenols and aroma in red wines from Portuguese mainland versus Azores Islands. *Food Research International*, 34, 345–355.
- Bardi, E., Koutinas, A. A., Psarianos, C., & Kanellaki, M. (1997). Volatile by-products formed in low-temperature wine-making using immobilized yeast cells. *Process Biochemistry*, 32, 579–584.
- Bellesia, F., Pinetti, A., Pagnoni, U. M., Rinaldi, R., Zucchi, C., Caglioti, L., et al. (2003). Volatile components of Grana Parmigiano-Reggiano type hard cheese. *Food Chemistry*, 83, 55–61.
- Berna, A. Z., Lammertyn, J., Saevels, S., Natale, C., & Nicolai, B. M. (2004). Electronic nose systems to study shelf life and cultivar effect on tomato aroma profile. *Sensors and Actuators B*, 97, 324–333.
- Bhattacharjee, P., Singhal, R. S., Gholap, A. S., Variyar, P. S., & Bongirwar, D. R. (2003). Hydrocarbons as marker compounds for irradiated cashew nuts. *Food Chemistry*, 80, 151–157.
- Bicchi, C., Cordero, C., Iori, C., & Rubiolo, P. (2000). Headspace sorptive extraction (HSSE) in the headspace analysis of aromatic and medicinal plants. *Journal of High Resolution Chromatography*, 23, 539–546.
- Bintsis, T., & Robinson, R. K. (2004). A study of the effects of adjunct cultures on the aroma compounds of Feta-type cheese. *Food Chemistry*, 88, 435–441.
- Biswas, S., Heindselmen, K., Wohltjen, H., & Staff, C. (2004). Differentiation of vegetable oils and determination of sunflower oil oxidation using a surface acoustic wave sensing device. *Food Control*, 15, 19–26.
- Blixt, Y., & Borch, E. (1999). Using an electronic nose for determining the spoilage of vacuum-packed beef. *International Journal of Food Microbiology*, 46, 123–134.
- Boido, E., Lloret, A., Medina, K., Fariña, L., Carrau, F., Versini, G., et al. (2003). Aroma composition of vitis vinifera cv. Tannat: the typical red wine from Uruguay. *Journal of Agricultural and Food Chemistry*, 51, 5408–5413.
- Bonino, M., Schellino, R., Rizzi, C., Aigotti, R., Delfini, C., & Baiocchi, C. (2003). Aroma compounds of an Italian wine (Ruché) by HS-SPME analysis coupled with GC-ITMS. *Food Chemistry*, 80, 125–133.
- Borse, B. B., Rao, L. J. M., Nagalakshmi, S., & Krishnamurthy, N. (2002). Fingerprint of black teas from India: identification of the region-specific characteristics. *Food Chemistry*, 79, 419–424.
- Boscaini, E., Mikoviny, T., Wisthaler, A., Hartungen, E., & Märk, T. D. (2004). Characterization of wine with PTR-MS. *International Journal of Mass Spectrometry*, 239, 215–219.
- Boudhrioua, N., Giampaoli, P., & Bonazzi, C. (2003). Changes in aromatic components of banana during ripening and air-drying. *Lebensmittel-Wissenschaft und-Technologie*, 36, 633–642.
- Brunton, N. P., Cronin, D. A., Monahan, F. J., & Durcan, R. (2000). A comparison of solid-phase microextraction (SPME) fibres for measurement of hexanal and pentanal in cooked turkey. *Food Chemistry*, 68, 339–345.
- Cai, J., Liu, B., & Su, Q. (2001). Comparison of simultaneous distillation extraction and solid-phase microextraction for the determination of volatile flavor components. *Journal of Chromatography A*, 930, 1–7.
- Carrasco, A., Tárrega, R., Ramirez, M. R., Mingoarranz, F. J., & Cava, R. (2005). Colour and lipid oxidation changes in dry-cured loins from free-range reared and intensively reared pigs as affected by ionizing radiation dose level. *Meat Science*, 69, 609–615.
- Castro, R., Natera, R., Benitez, P., & Barosso, C. G. (2004). Comparative analysis of volatile compounds of 'fino' sherry wine by rotatory and continuous liquid-liquid extraction and solid-phase microextraction in conjunction with gas chromatography-mass spectrometry. *Analytica Chimica Acta*, 513, 141–150.
- Cavalli, J.-F., Fernandez, X., Lizzani-Cuvelier, L., & Loiseau, A.-M. (2004). Characterization of volatile compounds of French and Spanish virgin olive oils by HS-SPME: identification of quality-freshness markers. *Food Chemistry*, 88, 151–157.
- Clemente-Jimenez, J. M., Mingorance-Cazorla, L., Martinez-Rodriguez, S., Heras-Vázquez, F. J., & Rodriguez-Vico, F. (2004). Molecular characterization and oenological properties of wine yeasts isolated during spontaneous fermentation of six varieties of grape must. *Food Microbiology*, 21, 149–155.
- Contarini, G., & Povolò, M. (2002). Volatile fraction of milk: comparison between purge and trap and solid phase microextraction techniques. *Journal of Agricultural and Food Chemistry*, 50, 7350–7355.
- Cortés, S., Gil, M. L., & Fernández, E. (2005). Volatile composition of traditional and industrial Orujo spirits. *Food Control*, 16, 383–388.
- Czapski, J., Grajek, W., & Pospiech, E. (1999). *Surowce, technologia i dodatki a jakośc żywności* (pp. 143–165). Poznań: Wydawnictwo Akademii Rolniczej w Poznaniu.
- D'Arcy, B. R., Rintoul, G. B., Rowland, C. Y., & Blackman, A. J. (1997). Composition of Australian honey extractives. I. Norisoprenoids, monoterpenes, and other natural volatiles from Blue Gum (*Eucalyptus leucoxylon*) and Yellow Box (*Eucalyptus melliodora*) honeys. *Journal of Agricultural and Food Chemistry*, 45, 1834–1843.
- D'Auria, M., Emanuele, L., Mauriello, G., & Racioppi, R. (2003). On the origin of "Goût de Lumière" in champagne. *Journal of Photochemistry and Photobiology A: Chemistry*, 158, 21–26.
- Dahl, S., Tavaría, F. K., & Malcata, F. X. (2000). Relationships between flavour and microbiological profiles in Sierra da Estrela cheese throughout ripening. *International Dairy Journal*, 10, 255–262.
- Demyttenaere, J. C. R., Dagher, C., Sandra, P., Kallithraka, S., Verhé, R., & Kimpe, N. (2003). Flavour analysis of Greek white wine by solid-phase microextraction-capillary gas chromatography-mass spectrometry. *Journal of Chromatography A*, 985, 233–246.
- Demyttenaere, J. C. R., Sánchez Martínez, J. I., Verhé, R., Sandra, P., & Kimpe, N. (2003). Analysis of volatiles of malt whisky by solid-phase microextraction and stir bar sorptive extraction. *Journal of Chromatography A*, 985, 221–232.
- Diéguez, S. C., Diaz, L. D., Peña, M. L. G., & Gómez, E. F. (2002). Variation of volatile organic acids in spirits during storage at low and room temperatures. *Lebensmittel-Wissenschaft und-Technologie*, 35, 452–457.
- Diéguez, S. C., Peña, M. L. G., & Gómez, E. F. (2003). Approaches to spirit aroma: contribution of some aromatic compounds to the primary aroma in samples of Orujo spirits. *Journal of Agricultural and Food Chemistry*, 51, 7385–7390.
- Dirinck, P., Opstaele, F., & Vandendriessche, F. (1997). Flavour differences between northern and southern European cured hams. *Food Chemistry*, 59, 511–529.
- Dirinck, P., & Winne, A. (1999). Flavour characterization and classification of cheeses by gas chromatographic-mass spectrometric profiling. *Journal of Chromatography A*, 847, 203–208.
- Dittmann, B., Zimmermann, B., Engelen, C., Jany, G., & Nitz, S. (2000). Use of the MS-sensor to discriminate between different dosages of garlic flavoring in tomato sauce. *Journal of Agricultural and Food Chemistry*, 48, 2887–2892.
- Dixon, J., & Hewett, E. W. (2001). Temperature of hypoxic treatment alters volatile composition of juice from 'Fuji' and 'Royal Gala' apples. *Postharvest Biology and Technology*, 22, 71–83.
- Doleschall, F., Kemény, Z., Recseg, K., & Kövári, K. (2001). Monitoring of lipid degradation products by solid-phase microextraction. *Journal of Microcolumn Separations*, 13, 215–220.
- Elmore, J. S., Mottram, D. S., & Hierro, E. (2000). Two-fibre solid-phase microextraction combined with gas chromatography-mass spectrometry

- for the analysis of volatile aroma compounds in cooked pork. *Journal of Chromatography A*, 905, 233–240.
- Falqué, E., Fernández, E., & Dubourdieu, D. (2002). Volatile components of Loureira, Dona Branca, and Treixadura wines. *Journal of Agricultural and Food Chemistry*, 50, 538–543.
- Farkaš, P., Sádecká, J., Kováč, M., Siegmunt, B., Leitner, E., & Pfannhauser, W. (1997). Key odourants of pressure-cooked hen meat. *Food chemistry*, 60, 617–621.
- Fenaille, F., Visani, P., Fumeaux, R., Milo, C., & Guy, P. A. (2003). Comparison of mass spectrometry-based electronic nose and solid phase microextraction gas chromatography-mass spectrometry technique to assess infant formula oxidation. *Journal of Agricultural and Food Chemistry*, 51, 2790–2796.
- Fernando, L. N., Berg, E. P., & Grün, I. U. (2003). Quantitation of hexanal by automated SPME for studying dietary influences on the oxidation of pork. *Journal of Food Composition and Analysis*, 16, 179–188.
- Ferrari, G., Lablanquie, O., Cantagrel, R., Ledauphin, J., Payot, T., Fournier, N., et al. (2004). Determination of key odorant compounds in freshly distilled cognac using GC-O, GC-MS, and sensory evaluation. *Journal of Agricultural and Food Chemistry*, 52, 5670–5676.
- Ferreira, V., Aznar, M., López, R., & Cacho, J. (2001). Quantitative gas chromatography-olfactometry carried out at different dilutions of an extract. Key differences in the odor profiles of four high-quality Spanish aged red wines. *Journal of Agricultural and Food Chemistry*, 49, 4818–4824.
- Ferreira, B., Hory, C., Bard, M. H., Taisant, C., Olsson, A., & Fur, Y. (1995). Effects of skin contact and settling on the level of the C18:2, C18:3 fatty acids and C6 compounds in Burgundy chardonnay musts and wines. *Food Quality and Preference*, 6, 35–41.
- Ferreira, V., Ortin, N., Escudero, A., López, R., & Cacho, J. (2002). Chemical characterization of the aroma of Grenache rosé wines: aroma extract dilution analysis, quantitative determination, and sensory reconstruction studies. *Journal of Agricultural and Food Chemistry*, 50, 4048–4054.
- Frank, D. C., Owen, C. M., & Patterson, J. (2004). Solid phase microextraction (SPME) combined with gas-chromatography and olfactometry-mass spectrometry for characterization of cheese aroma compounds. *Lebensmittel-Wissenschaft und-Technologie*, 37, 139–154.
- Freitas, A. M. C., Parreira, C., & Vilas-Boas, L. (2001). The use of an electronic aroma-sensing device to assess coffee differentiation-comparison with SPME gas chromatography-mass spectrometry aroma patterns. *Journal of Food Composition and Analysis*, 14, 513–522.
- Garcia, D. C., Reichenbacher, M., Danzer, K., Hurlbeck, C., Bartsch, C., & Feller, K.-H. (1998). Analysis of wine bouquet components using headspace solid-phase microextraction-capillary gas chromatography. *Journal of High Resolution Chromatography*, 21, 373–377.
- Girard, B., & Lau, O. L. (1995). Effect of maturity and storage on quality and volatile production of 'Jonagold' apples. *Food Research International*, 28, 465–471.
- González-Martin, I., Pérez-Pavón, J. L., González-Pérez, C., Hernández-Méndez, J., & Álvarez-García, N. (2000). Differentiation of products derived from Iberian breed swine by electronic olfactometry (electronic nose). *Analytica Chimica Acta*, 424, 279–287.
- Grabowska, J. (1994). Substancje zapachowe. In Z. E. Sikorski (Ed.), *Chemiczne i funkcjonalne właściwości składników żywności* (pp. 427–460). Warszawa: Wydawnictwo Naukowo-Techniczne.
- Grison-Pigé, L., Hossaert-McKey, M., Greeff, J. M., & Bessière, J.-M. (2002). Fig volatile compounds—a first comparative study. *Phytochemistry*, 61, 61–71.
- Guadarrama, A., Fernández, J. A., Íñiguez, M., Souto, J., & Saja, J. A. (2000). Array of conducting polymer sensors for the characterisation of wines. *Analytica Chimica Acta*, 411, 193–200.
- Guadarrama, A., Fernández, J. A., Íñiguez, M., Souto, J., & Saja, J. A. (2001). Discrimination of wine aroma using an array of conducting polymer sensors in conjunction with solid-phase microextraction (SPME) technique. *Sensors and Actuators B*, 77, 401–408.
- Guth, H. (1997). Quantitation and sensory studies of character impact odorants of different white wine varieties. *Journal of Agricultural and Food Chemistry*, 45, 3027–3032.
- Guyot, C., Bouseta, A., Scheirman, V., & Collin, S. (1998). Floral origin markers of chestnut and lime tree honeys. *Journal of Agricultural and Food Chemistry*, 46, 625–633.
- Guyot, C., Scheirman, V., & Collin, S. (1999). Floral origin markers of heather honeys: *Calluna vulgaris* and *Erica arborea*. *Food Chemistry*, 64, 3–11.
- Hernández-Gómez, L. F., Úbeda, J., & Briones, A. (2003). Melon fruit distillates: comparison of different distillation methods. *Food Chemistry*, 82, 539–543.
- Hernández-Gómez, L. F., Úbeda-Iranzo, J., Garcia-Romero, E., & Briones-Pérez, A. (2005). Comparative production of different melon distillates: chemical and sensory analyses. *Food Chemistry*, 90, 115–125.
- Hierro, E., Hoz, L., & Ordóñez, J. A. (2004). Headspace volatile compounds from salted and occasionally smoked dried meats (cecinas) as affected by animal species. *Food Chemistry*, 85, 649–657.
- Hill, P. G., & Smith, R. M. (2000). Determination of sulphur compounds in beer using headspace solid-phase microextraction and gas chromatographic analysis with pulsed flame photometric detection. *Journal of Chromatography A*, 872, 203–213.
- Ibáñez, E., López-sebastián, S., Ramos, E., Tabera, J., & Reglero, G. (1998). Analysis of volatile fruit components by headspace solid-phase microextraction. *Food Chemistry*, 63, 281–286.
- Iersel, M. F. M., Dieren, B., Rombouts, F. M., & Abee, T. (1999). Flavor formation and cell physiology during the production of alcohol-free beer with immobilized *Saccharomyces cerevisiae*. *Enzyme and Microbial Technology*, 24, 407–411.
- Janiček, G., Pokorný, J., & Davidek, J. (1977). *Chemia żywności*. Warszawa: Wydawnictwo Naukowo-Techniczne.
- Jeleń, H. H., Wlazły, K., Wąsowicz, E., & Kamiński, E. (1998). Solid-phase microextraction for the analysis of some alcohols and esters in beer: comparison with static headspace method. *Journal of Agricultural and Food Chemistry*, 46, 1469–1473.
- Jia, M., Zhang, Q. H., & Min, D. B. (1999). Pulsed electric field processing effects on flavor compounds and microorganisms of orange juice. *Food Chemistry*, 65, 445–451.
- Jiménez, A., Beltrán, G., & Aguilera, M. P. (2004). Application of solid-phase microextraction to the analysis of volatile compounds in virgin olive oils. *Journal of Chromatography A*, 1028, 321–324.
- Kanavouras, A., Kiritsakis, A., & Hernandez, R. J. (2005). Comparative study on volatile analysis of extra virgin olive oil by dynamic headspace and solid phase micro-extraction. *Food Chemistry*, 90, 69–79.
- Kataoka, H., Lord, H. L., & Pawliszyn, J. (2000). Applications of solid-phase microextraction on food analysis. *Journal of Chromatography A*, 880, 35–62.
- Keusgen, M., Schulz, H., Glodek, J., Krest, I., Krüger, H., Herchert, N., et al. (2002). Characterization of some *Allium* hybrids by aroma precursors, aroma profiles, and alliinase activity. *Journal of Agricultural and Food Chemistry*, 50, 2884–2890.
- Kłowski, G., Czupryński, B., Kotarska, K., & Wolska, M. (2003). Charakterystyka zanieczyszczeń chemicznych obniżających jakość spirytusu surowego (2). *Przemysł Fermentacyjny i Owocowo-Warzywny*, 9, 37–38.
- Kocsis, N., Amtmann, M., Mednyánszky, Z., & Korány, K. (2002). GC-MS investigation of the aroma compounds of Hungarian red paprika (*Capsicum annum* cultivars). *Journal of Food Composition and Analysis*, 15, 195–203.
- Lavilla, T., Recasens, I., Lopez, M. L., & Puy, J. (2002). Multivariate analysis of maturity stages, including quality and aroma, in 'Royal Glory' peaches and 'Big Top' nectarines. *Journal of the Science of Food and Agriculture*, 82, 1842–1849.
- Ledauphin, J., Saint-Clair, J.-F., Lablanquie, O., Guichard, H., Fournier, N., Guichard, E., et al. (2004). Identification of trace volatile compounds in freshly distilled calvados and cognac using preparative

- separations coupled with gas chromatography-mass spectrometry. *Journal of Agricultural and Food Chemistry*, 52, 5124–5134.
- Legin, A., Rudnitskaya, A., Lvova, L., Vlasov, Y., Natale, C., & D'Amico, A. (2003). Evaluation of Italian wine by the electronic tongue: recognition, quantitative analysis and correlation with human sensory perception. *Analytica Chimica Acta*, 484, 33–44.
- Ligor, M., & Buszewski, B. (1999). Determination of menthol and menthone in food and pharmaceutical products by solid-phase microextraction-gas chromatography. *Journal of Chromatography A*, 847, 161–169.
- Liu, M., Zeng, Z., & Xiong, B. (2005). Preparation of novel solid-phase microextraction fibers by sol-gel technology for headspace solid-phase microextraction-gas chromatographic analysis of aroma compounds in beer. *Journal of Chromatography A*, 1065, 287–299.
- Lorenzo, I. M., Pavón, J. L. P., Laespada, M. E. F., Pinto, C. G., & Cordero, B. M. (2002). Detection of adulterants in olive oil by headspace-mass spectrometry. *Journal of Chromatography A*, 945, 221–230.
- Lurie, S., Pre-Aymard, C., Ravid, U., Larkov, O., & Fallik, E. (2002). Effect of 1-methylcyclopropene on volatile emission and aroma in cv. Anna apples. *Journal of Agricultural and Food Chemistry*, 50, 4251–4256.
- Lyw, D., Gariépy, Y., Raghavan, G. S. V., & Kushalappa, A. C. (2001). Changes in volatile production during an infection of potatoes by *Erwinia carotovora*. *Food Research International*, 34, 807–813.
- Machiels, D., & Istasse, L. (2003). Evaluation of two commercial solid-phase microextraction fibres for the analysis of target aroma compounds in cooked beef meat. *Talanta*, 61, 529–537.
- Madrera, R. R., Gomis, D. B., & Alonso, J. J. M. (2003a). Influence of distillation system, oak wood type, and aging time on volatile compounds of cider brandy. *Journal of Agricultural and Food Chemistry*, 51, 5709–5714.
- Madrera, R. R., Gomis, D. B., & Alonso, J. J. M. (2003b). Influence of distillation system, oak wood type, and aging time on composition of cider brandy in phenolic and furanic compounds. *Journal of Agricultural and Food Chemistry*, 51, 7969–7973.
- Maicas, S., Gil, J.-V., Pardo, I., & Ferrer, S. (1999). Improvement of volatile composition of wines by controlled addition of malolactic bacteria. *Food Research International*, 32, 491–496.
- Mallouchos, A., Komaitis, M., Koutinas, A., & Kanellaki, M. (2002). Investigation of volatiles evolution during the alcoholic fermentation of grape must using free and immobilized cells with the help of solid phase microextraction (SPME) headspace sampling. *Journal of Agricultural and Food Chemistry*, 50, 3840–3848.
- Mallouchos, A., Komaitis, M., Koutinas, A., & Kanellaki, M. (2003a). Evolution of volatile by-products during wine fermentations using immobilized cells on grape skins. *Journal of Agricultural and Food Chemistry*, 51, 2402–2408.
- Mallouchos, A., Komaitis, M., Koutinas, A., & Kanellaki, M. (2003b). Wine fermentations by immobilized and free cells at different temperatures. Effect of immobilization and temperature on volatile by-products. *Food Chemistry*, 80, 109–113.
- Marco, A., Navarro, J. L., & Flores, M. (2004). Volatile compounds of dry-fermented sausages as affected by solid-phase microextraction (SPME). *Food Chemistry*, 84, 633–641.
- Marengo, E., Aceto, M., & Maurino, V. (2001). Classification of Nebbiolo-based wines from Piedmont (Italy) by means of solid-phase microextraction-gas chromatography-mass spectrometry of volatile compounds. *Journal of Chromatography A*, 943, 123–137.
- Mariaca, R., & Bosset, J. O. (1997). Instrumental analysis of volatile (flavour) compounds in milk and dairy products. *Lait*, 77, 13–40.
- Marsili, R. T. (1999). SPME-MS-MVA as an electronic nose for the study of off-flavors in milk. *Journal of Agricultural and Food Chemistry*, 47, 648–654.
- Martin, Y. G., Oliveros, M. C. C., Pavón, J. L. P., Pinto, C. G., & Cordero, B. M. (2001). Electronic nose based on metal oxide semiconductor sensors and pattern recognition techniques: characterisation of vegetable oils. *Analytica Chimica Acta*, 449, 69–80.
- Martin, Y. G., Pavón, J. L. P., Cordero, B. M., & Pinto, C. G. (1999). Classification of vegetable oils by linear discriminant analysis of Electronic Nose data. *Analytica Chimica Acta*, 384, 83–94.
- Martinez-Uruñuela, A., González-Siáz, J. M., & Pizarro, C. (2004). Optimisation of a headspace solid-phase microextraction method for the direct determination of chloroanisoles related to cork taint in red wine. *Journal of Chromatography A*, 1056, 49–56.
- Mateo, J. J., Jiménez, M., Pastor, A., & Huerta, T. (2001). Yeast starter cultures affecting wine fermentation and volatiles. *Food Research International*, 34, 307–314.
- Mazida, M. M., Salleh, M. M., & Osman, H. (2005). Analysis of volatile aroma compounds of fresh chilli (*Capsicum annum*) during stages of maturity using solid phase microextraction (SPME). *Journal of Food Composition and Analysis*, 18, 427–437.
- Mejias, R. C., Marin, R. N., Moreno, M. V. G., & Barroso, C. G. (2003). Optimisation of headspace solid-phase microextraction for the analysis of volatile phenols in wine. *Journal of Chromatography A*, 995, 11–20.
- Mestres, M., Busto, O., & Guasch, J. (1998). Headspace solid-phase microextraction analysis of volatile sulphides and disulphides in wine aroma. *Journal of Chromatography A*, 808, 211–218.
- Mielle, P. (1996). Electronic noses: towards the objective instrumental characterization of food aroma. *Trends in Food Science & Technology*, 7, 432–438.
- Mielle, P., & Marquis, F. (1999). An alternative way to improve the sensitivity of electronic olfactometers. *Sensors and Actuators B*, 58, 526–535.
- Mildner-Szkudlarz, S., Jeleń, H. H., Zawirska-Wojtasiak, R., & Wąsowicz, E. (2003). Application of headspace—solid phase microextraction and multivariate analysis for plant oils differentiation. *Food Chemistry*, 83, 515–522.
- Morcuende, D., Estévez, M., Ruiz, J., & Cava, R. (2003). Oxidative and lipolytic deterioration of different muscles from free-range reared Iberian pigs under refrigerated storage. *Meat Science*, 65, 1157–1164.
- Mpelasoka, B. S., & Behboudian, M. H. (2002). Production of aroma volatiles in response to deficit irrigation and to crop load in relation to fruit maturity for 'Braeburn' apple. *Postharvest Biology and Technology*, 24, 1–11.
- Muriel, E., Antequera, T., Petró, M. J., Andrés, A. I., & Ruiz, J. (2004). Volatile compounds in Iberian dry-cured loin. *Meat Science*, 68, 391–400.
- Nakai, S., Wang, Z. H., Dou, J., Nakamura, S., Ogawa, M., Nakai, E., et al. (1999). Gas chromatography/principal component similarity system for detection of *E. coli* and *S. aureus* contaminating salmon and hamburger. *Journal of Agricultural and Food Chemistry*, 47, 576–583.
- Nascimento, R. F., Cardoso, D. R., Keukeleire, D., Lima-Neto, B. S., & Franco, D. W. (2000). Quantitative HPLC analysis of acids in Brazilian Cachaças and various spirits using fluorescence detection of their 9-anthrylmethyl esters. *Journal of Agricultural and Food Chemistry*, 48, 6070–6073.
- Ng, L.-K., Lafontaine, P., & Harnois, J. (2000). Gas chromatographic-mass spectrometric analysis of acids and phenols in distilled alcohol beverages. Application of anion-exchange disk extraction combined with in-vial elution and silylation. *Journal of Chromatography A*, 873, 29–38.
- Nielsen, J. H., Sørensen, B., Skibsted, L. H., & Bertelsen, G. (1997). Oxidation in pre-cooked minced pork as influenced by chill storage of raw muscle. *Meat Science*, 46, 191–197.
- Nonato, E. A., Carazza, F., Silva, F. C., Carvalho, C. R., & Cardeal, Z. L. (2001). A headspace solid-phase microextraction method for the determination of some secondary compounds of Brazilian sugar cane spirits by gas chromatography. *Journal of Agricultural and Food Chemistry*, 49, 3533–3539.
- Ogihara, H., Horimoto, Y., Wang, Z. H., Skura, B. J., & Nakai, S. (2000). Solid phase microextraction/gas chromatography of Salmonella-infected beef. *Journal of Agricultural and Food Chemistry*, 48, 2253–2259.
- Oliveira, A. M., Pereira, N. R., Marsaioli, A., Jr., & Augusto, F. (2004). Studies on the aroma of cupuassu liquor by headspace solid-phase

- microextraction and gas chromatography. *Journal of Chromatography A*, 1025, 115–124.
- Oliveros, M. C. C., Pavón, J. L. P., Pinto, C. G., Laespada, M. E. F., Cordero, B. M., & Forina, M. (2002). Electronic nose based on metal oxide semiconductor sensors as a fast alternative for the detection of adulteration of virgin olive oils. *Analytica Chimica Acta*, 459, 219–228.
- Oshita, S., Shima, K., Haruta, T., Seo, Y., Kawagoe, Y., Nakayama, S., et al. (2000). Discrimination of odors emanating from 'La France' pear by semi-conducting polymer sensors. *Computers and Electronics in Agriculture*, 26, 209–216.
- Page, B. D., & Lacroix, G. (2000). Analysis of volatile contaminants in vegetable oils by headspace solid-phase microextraction with Carboxen-based fibres. *Journal of Chromatography A*, 873, 79–94.
- Paliyath, G., Whiting, M. D., Stasiak, M. A., Murr, D. P., & Clegg, B. S. (1997). Volatile production and fruit quality during development of superficial scald in Red Delicious apples. *Food Research International*, 30, 95–103.
- Park, Y. J., Kim, K. R., & Kim, J. H. (1999). Gas chromatographic organic acid profiling analysis of brandies and whiskeys for pattern recognition analysis. *Journal of Agricultural and Food Chemistry*, 47, 2322–2326.
- Patel, S., & Shibamoto, T. (2002). Effect of different strains of *Saccharomyces cerevisiae* on production of volatiles in Napa Gamay wine and Petite Sirah wine. *Journal of Agricultural and Food Chemistry*, 50, 5649–5653.
- Pawliszyn, J. (1997). *Solid phase microextraction: theory and practice*. New York: Wiley-VCH.
- Peña, F., Cárdenas, S., Gallego, M., & Valcárcel, M. (2004). Direct screening of olive oil samples for residual benzene hydrocarbon compounds by headspace-mass spectrometry. *Analytica Chimica Acta*, 526, 77–82.
- Penza, M., & Cassano, G. (2004a). Chemometric characterization of Italian wines by thin-film multisensors array and artificial neural networks. *Food Chemistry*, 86, 283–296.
- Penza, M., & Cassano, G. (2004b). Recognition of adulteration of Italian wines by thin-film multisensor array and artificial neural networks. *Analytica Chimica Acta*, 509, 159–177.
- Penza, M., Cassano, G., Tortorella, F., & Zaccaria, G. (2001). Classification of food, beverages and perfumes by WO₃ thin film sensors array and pattern recognition techniques. *Sensors and Actuators B*, 73, 76–87.
- Pèrès, C., Begnaud, F., & Berdagué, J.-L. (2002). Fast characterization of Camembert cheeses by static headspace-mass spectrometry. *Sensors and Actuators B*, 87, 491–497.
- Pèrès, C., Denoyer, C., Tournayre, P., & Berdagué, J.-L. (2002). Fast characterization of cheeses by dynamic headspace-mass spectrometry. *Analytical Chemistry*, 74, 1386–1392.
- Pèrès, C., Viallon, C., & Berdagué, J.-L. (2001). Solid-phase microextraction-mass spectrometry: a new approach to the rapid characterization of cheeses. *Analytical Chemistry*, 73, 1030–1036.
- Pillonel, L., Bosset, J. O., & Tabacchi, R. (2002). Rapid preconcentration and enrichment techniques for the analysis of food volatile. A review. *Lebensmittel-Wissenschaft und-Technologie*, 35, 1–14.
- Pino, J., Martí, M. P., Mestres, M., Pérez, J., Busto, O., & Guasch, J. (2002). Headspace solid-phase microextraction of higher fatty acid ethyl esters in white rum aroma. *Journal of Chromatography A*, 954, 51–57.
- Pollien, P., Ott, A., Montigon, F., Baumgartner, M., Muñoz-Box, R., & Chaintreau, A. (1997). Hyphenated headspace-gas chromatography-sniffing technique: screening of impact odorants and quantitative aromagram comparisons. *Journal of Agricultural and Food Chemistry*, 45, 2630–2637.
- Polychroniadou, E., Kanellaki, M., Iconomopoulou, M., Koutinas, A. A., Marchant, R., & Banat, I. M. (2003). Grape and apple wines volatile fermentation products and possible relation to spoilage. *Bioresource Technology*, 87, 337–339.
- Porto, C., Pizzale, L., Bravin, M., & Conte, L. S. (2003). Analyses of orange spirit flavour by direct-injection gas chromatography-mass spectrometry and headspace solid-phase microextraction/GC-MC. *Flavour and Fragrance Journal*, 18, 66–72.
- Povolo, M., & Contarini, G. (2003). Comparison of solid-phase microextraction and purge-and-trap methods for the analysis of the volatile fraction of butter. *Journal of Chromatography A*, 985, 117–125.
- Quach, M., Chen, X. D., & Stevenson, R. J. (1999). Headspace sampling of whey protein concentrate solutions using solid-phase microextraction. *Food Research International*, 31, 371–379.
- Radovic, B. S., Careri, M., Mangia, A., Musci, M., Gerboles, M., & Anklam, E. (2001). Contribution of dynamic headspace GC-MS analysis of aroma compounds to authenticity testing of honey. *Food Chemistry*, 72, 511–520.
- Reed, K. A., Sims, C. A., Gorbet, D. W., & O'Keefe, S. F. (2002). Storage water activity affects flavor fade in high and normal oleic peanuts. *Food Research International*, 35, 769–774.
- Refsgaard, H. H. F., Haahr, A.-M., & Jensen, B. (1999). Isolation and quantification of volatiles in fish by dynamic headspace sampling and mass spectrometry. *Journal of Agricultural and Food Chemistry*, 47, 1114–1118.
- Roberts, D. D., Pollien, P., & Milo, C. (2000). Solid-phase microextraction method development for headspace analysis of volatile flavor compounds. *Journal of Agricultural and Food Chemistry*, 48, 2430–2437.
- Rocha, S., Coutinho, P., Barros, A., Coimbra, M. A., Delgadillo, I., & Cardoso, A. D. (2000). Aroma potential of two Bairrada white grape varieties: Maria Gomes and Bical. *Journal of Agricultural and Food Chemistry*, 48, 4802–4807.
- Rodríguez-Bencomo, J. J., Conde, J. E., Rodríguez-Delgado, M. A., García-Montelongo, F., & Pérez-Trujillo, J. P. (2002). Determination of esters in dry and sweet white wines by headspace solid-phase microextraction and gas chromatography. *Journal of Chromatography A*, 963, 213–223.
- Ruiz, J., Ventanas, J., & Cava, R. (2001). New device for direct extraction of volatiles in solid samples using SPME. *Journal of Agricultural and Food Chemistry*, 49, 5115–5121.
- Ruth, S. M., Roozen, J. P., Cozijnsen, J. L., & Posthumus, M. A. (1995). Volatile compounds of rehydrated French beans, bell peppers and leeks. Part II. Gas chromatography/sniffing port analysis and sensory evaluation. *Food Chemistry*, 54, 1–7.
- Ryan, D., Shellie, R., Tranchida, P., Casilli, A., Mondello, L., & Marriott, P. (2004). Analysis of roasted coffee bean volatiles by using comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry. *Journal of Chromatography A*, 1054, 57–65.
- Rychlik, M., & Grosch, W. (1996). Identification and quantification of potent odorants formed by toasting of wheat bread. *Lebensmittel-Wissenschaft und-Technologie*, 29, 515–525.
- Sabarez, H. T., Price, W. E., & Korth, J. (2000). Volatile changes during dehydration of d'Agen prunes. *Journal of Agricultural and Food Chemistry*, 48, 1838–1842.
- Sala, C., Mestres, M., Martí, M. P., Busto, O., & Guasch, J. (2000). Headspace solid-phase microextraction method for determining 3-alkyl-2-methoxy-pyrazines in musts by means of polydimethylsiloxane-divinylbenzene fibres. *Journal of Chromatography A*, 880, 93–99.
- Sala, C., Mestres, M., Martí, M. P., Busto, O., & Guasch, J. (2002). Headspace solid-phase microextraction analysis of 3-alkyl-2-methoxy-pyrazines in wines. *Journal of Chromatography A*, 953, 1–6.
- Sanches-Silva, A., Lopez-Hernández, J., & Paseiro-Losada, P. (2005). Profiling flavor compounds of potato crisps during storage using solid-phase microextraction. *Journal of Chromatography A*, 1064, 239–245.
- Sánchez-Peña, C. M., Luna, G., García-González, D. L., & Aparicio, R. (2005). Characterization of French and Spanish dry-cured hams: influence of the volatiles from the muscles and the subcutaneous fat quantified by SPME-GC. *Meat Science*, 69, 635–645.
- Sanchez-Silva, A., Quirós, A. R.-B., López-Hernández, J., & Paseiro-Losada, P. (2004). Determination of hexanal as indicator of the lipidic oxidation state in potato crisps using gas chromatography and high-performance liquid chromatography. *Journal of Chromatography A*, 1046, 75–81.

- Santos, J. P., Arroyo, T., Aleixandre, M., Lozano, J., Sayago, I., Garcia, M., et al. (2004). A comparative study of sensor array and GC–MS: application to Madrid wines characterization. *Sensors and Actuators B*, 102, 299–307.
- Sen, N. P., Seaman, S. W., & Page, B. D. (1997). Rapid semi-quantitative estimation of N-nitrosodibutylamine and N-nitrosodibenzylamine in smoked hams by solid-phase microextraction followed by gas chromatography-thermal energy analysis. *Journal of Chromatography A*, 788, 131–140.
- Servili, M., Selvaggini, R., Taticchi, A., Begliomini, A. L., & Montedoro, G. F. (2000). Relationships between the volatile compounds evaluated by solid phase microextraction and the thermal treatment of tomato juice: optimization of the blanching parameters. *Food Chemistry*, 71, 407–415.
- Servili, M., Selvaggini, R., Taticchi, A., Esposito, S., & Montedoro, G. (2003). Volatile compounds and phenolic composition of virgin olive oil: optimization of temperature and time of exposure of olive pastes to air contact during the mechanical extraction process. *Journal of Agricultural and Food Chemistry*, 51, 7980–7988.
- Shaw, P. E., Rouseff, R. L., Goodner, K. L., Bazemore, R., Nordby, H. E., & Widmer, W. W. (2000). Comparison of headspace GC and electronic sensor techniques for classification of processed orange juices. *Lebensmittel-Wissenschaft und-Technology*, 33, 331–334.
- Sides, A., Robards, K., & Helliwell, S. (2000). Developments in extraction techniques and their application to analysis of volatiles in foods. *Trends in Analytical Chemistry*, 19, 322–329.
- Siegmund, B., & Murkovic, M. (2004). Changes in chemical composition of pumpkin seeds during the roasting process for production of pumpkin seed oil (Part 2: volatile compounds). *Food Chemistry*, 84, 367–374.
- Silva, M. L., Malcata, F. X., & Revel, G. (1996). Volatile contents of grape marcs in Portugal. *Journal of Food Composition and Analysis*, 9, 72–80.
- Smyth, A. B., Song, J., & Cameron, A. C. (1998). Modified atmosphere packaged cut iceberg lettuce: effect of temperature and O₂ partial pressure on respiration and quality. *Journal of Agricultural and Food Chemistry*, 46, 4556–4562.
- Song, J., Gardner, B. D., Holland, J. F., & Beaudry, R. M. (1997). Rapid analysis of volatile flavor compounds in apple fruit using SPME and GC/time-of-flight mass spectrometry. *Journal of Agricultural and Food Chemistry*, 45, 1801–1807.
- Soria, A. C., González, M., Lorenzo, C., Martínez-Castro, I., & Sanz, J. (2004). Characterization of artisanal honeys from Madrid (Central Spain) on the basis of their melissopalynological, physicochemical and volatile composition data. *Food Chemistry*, 85, 121–130.
- Soufleros, E. H., Mygdalia, A. S., & Natskoulis, P. (2004). Characterization and safety evaluation of the traditional Greek fruit distillate “Mouro” by flavor compounds and mineral analysis. *Food Chemistry*, 86, 625–636.
- Spranger, M. I., Climaco, M. C., Sun, B., Eiriz, N., Fortunato, C., Nunes, A., et al. (2004). Differentiation of red winemaking technologies by phenolic and volatile composition. *Analytica Chimica Acta*, 513, 151–161.
- Stashenko, E. E., Puertas, M. A., Salgar, W., Delgado, W., & Martínez, J. R. (2000). Solid-phase microextraction with on-fibre derivatisation applied to the analysis of volatile carbonyl compounds. *Journal of Chromatography A*, 886, 175–181.
- Steffen, A., & Pawliszyn, J. (1996). Analysis of flavor volatiles using headspace solid-phase microextraction. *Journal of Agricultural and Food Chemistry*, 44, 2187–2193.
- Steine, C., Beaucois, F., Siv, C., & Peiffer, G. (2001). Potential of semiconductor sensor arrays for the origin authentication of pure Valencia orange juices. *Journal of Agricultural and Food Chemistry*, 49, 3151–3160.
- Supelco Bulletin 869A (1998). *Solid phase microextraction: solventless sample preparation for monitoring flavor compounds by capillary gas chromatography*.
- Supelco Bulletin 923 (1998). *Solid phase microextraction: theory and optimization of conditions*.
- Supelco Bulletin 929 (2001). *A practical guide to quantitation with solid phase microextraction*.
- Thierry, A., Maillard, M.-B., Hervé, C., Richoux, R., & Lortal, S. (2004). Varied volatile compounds are produced by *Propionibacterium freudenreichii* in Emmental cheese. *Food Chemistry*, 87, 439–446.
- Togari, N., Kobayashi, A., & Aishima, T. (1995). Pattern recognition applied to gas chromatographic profiles of volatile components in three tea categories. *Food Research International*, 28, 495–502.
- Torrea, D., Fraile, P., Garde, T., & Ancin, C. (2003). Production of volatile compounds in the fermentation of chardonnay musts inoculated with two strains of *Saccharomyces cerevisiae* with different nitrogen demands. *Food Control*, 14, 565–571.
- Triqui, H., & Bouchriti, N. (2003). Freshness assessments of Moroccan sardine (*Sardina pilchardus*): comparison of overall sensory changes to instrumentally determined volatiles. *Journal of Agricultural and Food Chemistry*, 51, 7540–7546.
- Tura, D., Prenzler, P. D., Bedgood, D. R., Jr., Antolovich, M., & Robards, K. (2004). Varietal and processing effects on the volatile profile of Australian olive oils. *Food Chemistry*, 84, 341–349.
- Tuszyński, T., & Tarko, T. (2000). Lotne komponenty C₆ w winach i innych napojach alkoholowych. *Przemysł Fermentacyjny i Owocowo-Warzywny*, 6, 18–21.
- Ulberth, F., & Roubicck, D. (1995). Monitoring of oxidative deterioration of milk powder by headspace gas chromatography. *International Dairy Journal*, 5, 523–531.
- Valero, E., Moyano, L., Millan, M. C., Medina, M., & Ortega, J. M. (2002). Higher alcohols and esters production by *Saccharomyces cerevisiae*. Influence of the initial oxygenation of the grape must. *Food Chemistry*, 78, 57–61.
- Vallejo-Cordoba, B., González-Córdova, A. F., & Estrada-Montoya, M. C. (2004). Tequila volatile characterization and ethyl ester determination by solid phase microextraction gas chromatography/mass spectrometry analysis. *Journal of Agricultural and Food Chemistry*, 52, 5567–5571.
- Versari, A., Natali, N., Russo, M. T., & Antonelli, A. (2003). Analysis of some Italian lemon liquors (Limoncello). *Journal of Agricultural and Food Chemistry*, 51, 4978–4983.
- Vianna, E., & Ebeler, S. E. (2001). Monitoring ester formation in grape juice fermentations using solid phase microextraction coupled with gas chromatography-mass spectrometry. *Journal of Agricultural and Food Chemistry*, 49, 589–595.
- Vichi, S., Castellote, A. I., Pizzale, L., Conte, L. S., Buxaderas, S., & López-Tamames, E. (2003). Analysis of virgin olive oil volatile compounds by headspace solid-phase microextraction coupled to gas chromatography with mass spectrometric and flame ionization detection. *Journal of Chromatography A*, 983, 19–33.
- Vichi, S., Pizzale, L., Conte, L. S., Buxaderas, S., & López-Tamames, E. (2003). Solid-phase microextraction in the analysis of virgin olive oil volatile fraction: modifications induced by oxidation and suitable markers of oxidative status. *Journal of Agricultural and Food Chemistry*, 51, 6564–6571.
- Wang, Z. H., Dou, J., Macura, D., Durance, T. D., & Nakai, S. (1998). Solid phase extraction for GC analysis of beany flavours in soymilk. *Food Research International*, 30, 503–511.
- Wardencki, W., Sowiński, P., & Curyło, J. (2003). Evaluation of headspace solid-phase microextraction for the analysis of volatile carbonyl compounds in spirits and alcoholic beverages. *Journal of Chromatography A*, 984, 89–96.
- Wasiak, M. (2000). Akroleina – powstawanie, występowanie i właściwości. *Przemysł Fermentacyjny i Owocowo-Warzywny*, 5, 22–24.
- Webster, L., Simpson, P., Shanks, A. M., & Moffat, C. F. (2000). The authentication of olive oil on the basis of hydrocarbon concentration and composition. *Analyst*, 125, 97–104.
- Wilkes, J. G., Conte, E. D., Kim, Y., Holcomb, M., Sutherland, J. B., & Miller, D. W. (2000). Sample preparation for the analysis of flavors and off-flavors in foods. *Journal of Chromatography A*, 880, 3–33.

- Williams, A., Ryan, D., Guasca, A. O., Marriott, P., & Pang, E. (2005). Analysis of strawberry volatiles using comprehensive two-dimensional gas chromatography with headspace solid-phase microextraction. *Journal of Chromatography B*, 817, 97–107.
- Wong, S., O'Reilly, J., & Pawliszyn, J. (2004). High throughput method for meat spoilage analysis: SPME with combiPAL automation. In www.bioscienceworld.ca/Therapeutics.html.
- Yang, X., & Peppard, T. (1994). Solid-phase microextraction for flavor analysis. *Journal of Agricultural and Food Chemistry*, 42, 1925–1930.
- Zhu, M., Aviles, F. J., Conte, E. D., Miller, D. W., & Perschbacher, P. W. (1999). Microwave mediated distillation with solid-phase microextraction: determination of off-flavors, geosmin and methylisoborneol, in catfish tissue. *Journal of Chromatography A*, 833, 223–230.
- Zierler, B., Siegmund, B., & Pfannhauser, W. (2004). Determination of off-flavour compounds in apple juice caused by microorganisms using headspace solid phase microextraction-gas chromatography-mass spectrometry. *Analytica Chimica Acta*, 520, 3–11.
- Zunin, P., Boggia, R., Lanteri, S., Leardi, R., Andreis, R., & Evangelisti, F. (2004). Direct thermal extraction and gas chromatographic-mass spectrometric determination of volatile compounds of extra-virgin olive oils. *Journal of Chromatography A*, 1023, 271–276.