Filbertone as a Marker for the Assessment of Hazelnut Spread Quality

Helena ČÍŽKOVÁ, Aleš RAJCHL, Jitka ŠNEBERGROVÁ and Michal VOLDŘICH

Department of Food Preservation, Faculty of Food and Biochemical Technology, Institute of Chemical Technology Prague, Prague, Czech Republic

Abstract

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A method was proposed for the authenticity evaluation of the hazelnut based products, in which the hazelnut paste content is the principle qualitative parameter. The procedure is based on the determination of filbertone ((*E*)-5-methylhept-2-en-4-one), the natural, unique, and characteristic aroma component of the hazelnuts. A set of authentic hazelnut pastes and model samples containing various hazelnut paste amounts (from 0.1% to 28%) were analysed. Due to the variability found in filbertone content, it was not possible to propose a sufficiently robust model for the hazelnut paste quantification, however, filbertone was found to be a proper marker for the quality sorting of commercial hazelnut spreads. Available hazelnut spreads from the market were analysed and classified into three groups: samples with minimal content of hazelnuts (less than 1%, the filbertone content lower than 4 μg/kg); samples with middle contents of hazelnuts (from 1% to 10%, filbertone 4–45 μg/kg); superior samples with high contents of hazelnuts (above 10%, filbertone above 45 μg/kg).

Keywords: *Corylus avellana* L.; 5-methylhept-2-en-4-one; volatile components; authenticity; quality; allergens

The basic hazelnut spread raw material is hazelnut paste (butter), a thick semi-solid product, consisting of hazelnut particles dispersed in hazelnut oil and ranging in size from 7 μm to 45 μm. Hazelnut paste is an important ingredient in the production of confections, bakery products, icings, fillings, and ice creams. It contributes to the specific flavour and rich taste, lowers the melting point of the product for creamier mouth feel, and adds extra nutritional value to the product. It is an excellence source of unsaturated lipids, proteins, dietary fiber, antioxidant phenolic compounds, and minerals (Bonvehi & Coll 2009).

The recipes for hazelnut spreads vary in different trademarks and countries. In addition to a certain amount of hazelnut paste, these products mainly consist of sugars, vegetable oils, and artificial flavourings. The quality and consumers' acceptance of hazelnut spreads are based on the content and composition of the hazelnut product used in their production. The benchmark for the hazelnut spreads is Nutella, which has generally become synonymous with hazelnut and chocolate spread worldwide, and similar products with other brand names containing from 10% to 20% of hazelnuts. However, there are also hazelnut spreads with the declared hazelnuts content of about 2%, and similar "spreads with hazelnut flavour" containing artificial hazelnut flavourings only or a very low content of hazelnuts ranging from 0% to 2%.

The methods for the analysis of the hazelnut content can be divided according to the purpose of such analyses: (*i*) to detect the presence of allergens; or to evaluate the authenticity of the hazel-

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nut products; (*ii*) to determine the not permitted hazelnut oil addition into olive oil possessing similar fatty acid composition.

The detection of lowering the hazelnut content in hazelnut products by "dilution" with the addition of other ingredients e.g. vegetable oil into the hazelnut paste, is based on the determination of the characteristic profile of fatty acids, triacylglycerols, contents of stigmas-3,5-diene and tocopherols, followed by subsequent statistical processing of the results. However, the use of chemometric approach is limited by the complexity of the hazelnut spread matrices, the high variability of hazelnut markers or their presence in extenders (Bonvehi & Coll 2009).

Among the promising methods, the chromatographic analyses of the volatile flavour compounds may be mentioned. Despite the high natural variability, in the volatiles profile of hazelnuts their origin is unique and undoubted. Hazelnut aroma depends on the cultivar, ripeness, climatic conditions, and roasting conditions. The impact compounds are produced by both biochemical and thermal pathways (Pfnuer *et al.* 1999). More than 70 compounds were detected in roasted hazelnuts, including the most abundant pyrazines (2,6-dimethylpyrazine, 2,3-dimethylpyrazine, 2-ethyl-3-methylpyrazine), carbonyl compounds (hexanal, 3-methylbutanal, 3-penten-2-one, 5-methyl-2-hepten-4-one), and furans (2-methyl-3-furanthiol, 2,3,5-trimethylfuran). Among others, filbertone, (*E*)-5-methyl-hept-2-en-4-one, has been reported as the primary odorant (nutty roasty, hazelnut like aroma) of roasted hazelnuts (Pfnuer *et al.* 1999; Alasalvar *et al.* 2003).

Filbertone naturally occurs in raw hazelnuts, but its content extensively increases during roasting. In a model experiment, the content of this compound increased at 180°C from 1.4 to 660 µg/kg in 9 min, and to 1150 µg/kg in 15 minutes. In fact, 315 µg/kg were found in commercially produced oil from roasted nuts, whereas oil from unroasted nuts contained less than 10 µg/kg of filbertone (Belitz *et al.* 2009). However, the very high temperature (4 h at to 250°C under nitrogen) reached during hazelnut oil deodorisation may theoretically lead to partial or even total removal of the volatile (b.p. 173°C) compounds (Castillo & Herraiz 2003).

Currently, filbertone is considered to be a marker for distinguishing olive oil adulterated with hazelnut oil (Blanch *et al.* 1998; Flores *et al.* 2006; Pavón *et al.* 2009). Hazelnut oil is significantly cheaper than olive oil, but routine analyses of fatty acids and sterols compositions fail due to their similar profiles in both oils (Maggio *et al.* 2010). The methods described for the detection of olive oil adulteration with hazelnut oil based on filbertone involve usually preconcentration steps (steam distillation-extraction, solid phase microextraction, ultrasonically assisted solid-phase extraction, and supercritical fluid extraction) and analyses on gas chromatograph equipped with programmable temperature vaporiser and/or mass spectrometer (MS) detector in the selected ion monitoring the acquisition mode to improve sensitivity. The detection limit generally ranges from 0.3 µg to 50 µg filbertone/l. It allows the recognition from 7% to 20% of hazelnut oil in olive oil, according to its variety, geographical origin, degree of refining, and methodology used (Flores *et al.* 2006; Pavón *et al.* 2009).

We suggested, in view of the experience with filbertone in adulterated olive oils, to take an advantage of the filbertone presence in hazelnut raw material for hazelnut spreads evaluation. The aim of the study was to verify the filbertone as the tool for the assessment of hazelnut spreads grading and to propose a method for the estimation of the hazelnut paste content in hazelnut spreads.

MATERIAL AND METHODS

Material. Five samples (marked A, B, C, D, and E) of hazelnuts paste were obtained from the local producer of hazelnut confectioneries, their designation and specification are given in Table 1.

Table 1. Specification and filbertone content in authentic hazelnut pastes

Sample	Declared content of hazelnuts (%)	Origin (area of hazelnuts cultivation)	Filbertone concentration (µg/kg)
A	100	Turkey	344
B	100	Italy	400
C	100	Italy	516
D	100	Italy	304
E	100	Turkey	584

A set of 30 model hazelnut spread samples of known compositions was prepared for the proposed methodology evaluation. From this set, 20 samples with known hazelnut paste contents (0.1, 5, 10, 13, and 28%, made from pastes A, D, and E), with typical composition of commercial spreads (sugar, vegetable oil, dried milk, cacao; the components were added in the ratio of 10:10:4:1, respectively), were prepared in the process laboratory of the producer. An analogous set of 10 test samples with known hazelnut paste contents (0.1, 5, 10, and 13%, made from pastes B and C) were prepared in the authors' laboratory. The employment of the individual pastes for preparing distinct spread samples and their contents are shown in Figure 2.

A set of 7 real (commercial) samples of hazelnut spreads with declared and undeclared hazelnut contents was purchased from the market.

Chemicals. The standard reference compound filbertone ((*E*)-5-methyl-hept-2-en-4-one, 98%) was purchased from Sigma-Aldrich Corp. (St. Louise, USA).

SPME/GC/MS procedure. The headspace solid phase microextraction (SPME) procedure was performed by CombiPal (CTC Analytics AG, Zwingen, Switzerland) and was modified according to Flores *et al.* (2006). The sample (0.1 g of the sample and 1.5 ml of NaCl saturated solution) was equilibrated for 10 min at 60°C. The extraction was carried out using 50/30 μm Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco Inc., Bellefonte, USA) inserted into the headspace of a 10 ml vial filled with the sample which was subsequently agitated at 500 rpm and 60°C for 5 minutes.

The analyses were performed by gas chromatography-mass spectrometry (GC/MS) on GC 6890N (Agilent Technologies, Santa Clara, USA) equipped with a quadrupole mass detector (MS 5973) and DB-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness; Agilent JW Scientific, Folsom, USA). The split (1:10) GC inlet was maintained at 250°C and desorption time of 2 min was used. The constant carrier gas (He) flow was 1.2 ml/minute. The temperature program was 60°C (5 min); 5°C/min; 80°C; 25°C/min; 250°C (2 min). Selected ion monitoring (SIM) acquisition mode (response monitored at *m/z* 69, 98, 111, and 126) was used for the detection.

RESULTS AND DISCUSSION

Optimisation of the analytical method

The evaluation of the volatile profiles or the determination of the unique volatile component concentration may serve as an inherent parameter for the quality evaluation or discrimination between the analysed samples, provided that suitable methods and comprehensive data from authentic sources are available (Rajchl *et al.* 2009).

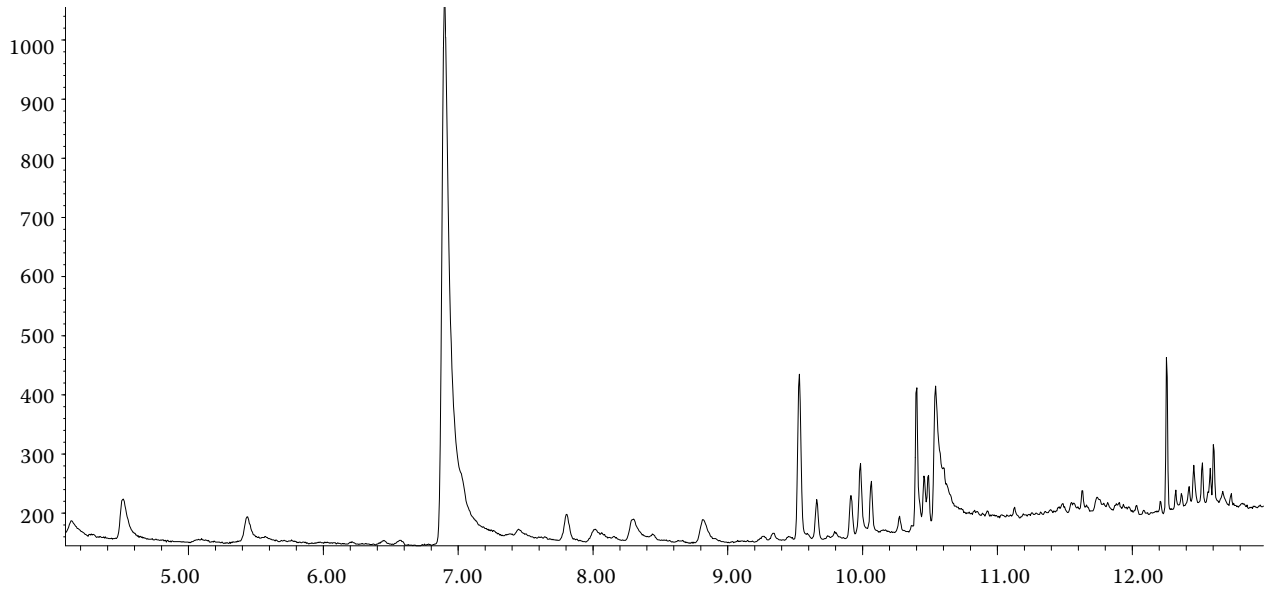

Figure 1. Example of chromatogram of model spreads with 10% of hazelnut paste, which corresponds to filbertone content of 34 μg/kg (filbertone in retention time 6.9 min)

The total ion current (TIC) mode of the described SPME/GC/MS method allowed the correct identification of more than 20 compounds in the volatile fraction of the hazelnut paste and hazelnut spread samples. The majority consisted of carbonyl compounds, alcohols, and pyrazines and corresponded fairly with the tabulated volatiles profile of roasted hazelnuts (Alasalvar *et al.* 2003). Thus, the obtained profiles could serve as the first screening to sort out the suspected or sensorially objectionable samples. However, the grading of hazelnut spreads was, due to the high natural variability of these fingerprints, infeasible and the research was subsequently focused on the content of the primary odorant of roasted hazelnuts – filbertone.

Compared to the other peaks in TIC, filbertone was very poorly represented and, moreover, overlaid with 2-ehtyl-3-methylpyrazine. To achieve a lower limit of detection and higher selectivity for filbertone as the target compound, SIM mode, in accordance with a literature reference (Flores *et al.* 2006), was used for subsequent testing.

An optimisation procedure was accomplished to select the experimental conditions most suitable for the determination of filbertone in hazelnut pastes and spreads. To this aim, several temperatures (20, 40, 60, and 70°C), extraction times (2, 5 and, 10 min), SPME fibers provided by Supelco Inc. (Bellefonte, USA) (100 µm PDMS, PDMS/DVB and PDMS/CAR/DVB), and sample weights (0.1 g and 1 g) were tested. These experimental conditions were followed to evaluate the relevant recoveries and repeatabilities. Based on this experimentation, the 50/30 µm DVB/CAR/PDMS fiber was selected as the best option because the other fibers provided once and 5 times lower sensitivity to filbertone as compared to that of the former. Next optimal values (the sample weight 0.1 g equilibrated for 10 min and extracted at 60°C add bracket for 5 min) were selected and are described in the Material and methods.

The recovery of filbertone obtained by spiking the nut (hazelnut-free) spread with 50 µg/kg and nut (hazelnut-free) paste with 500 µg/kg was 98% and 81%, respectively; the repeatability (RSD) was 8.1% and 11.2%, respectively. The limit of detection (LOD) was 2 µg/kg, the limit of quantification (LOQ) was 5 µg/kg, and the linearity range was 5–750 µg/kg (which relates to the calibration solution from 0.1 to 15 mg/l). Figure 1 shows an example of chromatogram of the model spread (A10) with 10% of hazelnut paste, which corresponds to filbertone (in retention time 7.1 min) concentration of 34 µg/kg.

Composition of raw material (hazelnut paste)

Hazelnut paste is a basic component of hazelnut spreads. It is prepared by grinding roasted hazelnuts to which sugar, vegetable oil, or suitable seasoning and stabilising ingredients may be added in the amount of about 10% of the weight of the final product. Table 1 shows that filbertone content varied greatly from paste to paste ranging from 304 µg/kg to 584 µg/kg, with a mean of 430 µg/kg and standard deviation ± 105 µg/kg. The results are in a good agreement with the contents of filbertone in hazelnut oils and roasted hazelnuts stated in the literature (Pfnuer *et al.* 1999; Belitz *et al.* 2009) where a high variability with the variety, roasting time, temperature, and storage conditions is mentioned. Moreover, in the case of hazelnut pastes, the undeclared addition of vegetable oils or other extenders can also decrease the filbertone content. The average value and variability obtained were used as the basis for our evaluation of the hazelnut paste contents in spreads.

Relationship between hazelnut paste and filbertone content

For the grading of hazelnut based products according to the hazelnut paste content, the linear regression was used to produce a single model. A training set of 30 samples of hazelnut spreads with the known hazelnut paste contents varying from 0.1 to 28% were analysed for the filbertone content (Figure 2). From this set, 20 samples were prepared by the same technology in the process laboratory of the producer, from three different hazelnut pastes (A, D, E), which are described in Table 1. Ten samples were prepared in the authors' laboratory from hazelnut pastes B and C.

The measured contents of filbertone were in the range from below the detection limit to 120 µg/kg. The correlation relationship between the relative hazelnut paste content (X, in %) and filbertone contents (Y, in µg/kg) was obtained: $Y = 4.21 \times X$, loaded with a relatively high correlation coefficient ($R = 0.944$) but with an unacceptable standard error of estimate ($\sigma_{est} = 12.5$).

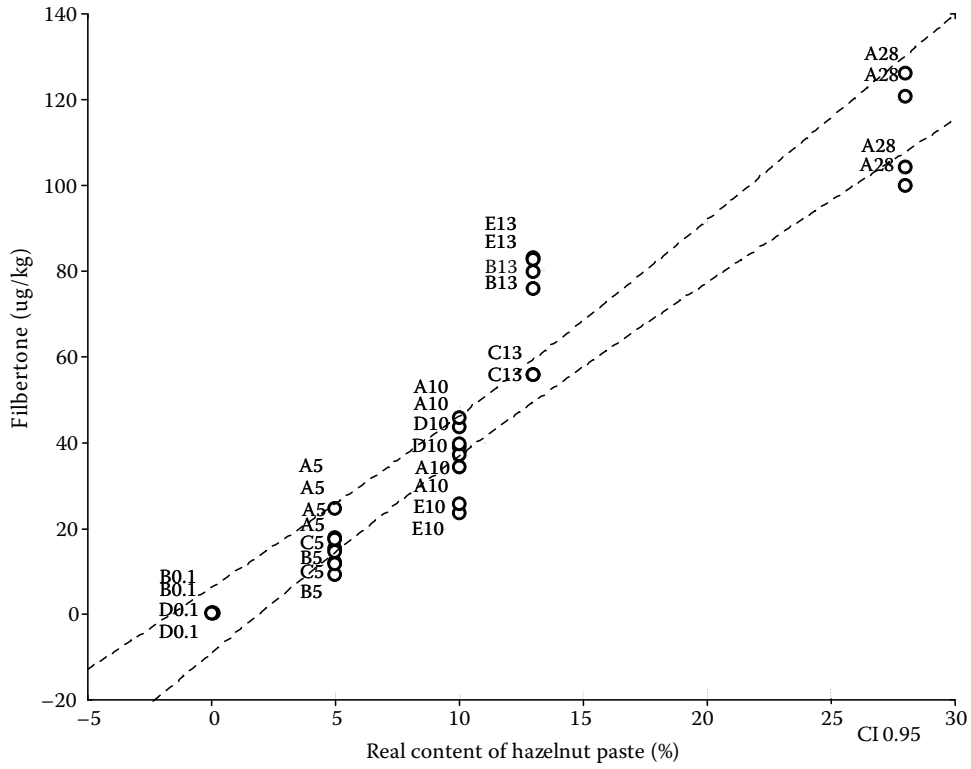

Figure 2. Correlation between real hazelnut paste content and filbertone content in 30 model samples of hazelnut spreads with known amount of hazelnut pastes (from 0.1% to 28 %), employment of individual pastes A, B, C, D, and E is marked

An insufficient robustness was caused by the use of a single marker, which is naturally variable in the dependence on the quality, origin, and roasting level of hazelnuts in the paste, and also on the changes in the preparation of spreads, when preconcentration contrary to the expected yield was observed in most cases. The error of the analytical method used must be also taken into consideration. It is evident that the exploitation of the above regression equation for the prediction of the hazelnut content in unknown samples is rather limited.

However, the proposed model allows sorting out the hazelnut spreads according to the filbertone content, with the accuracy of classification in agreement with the categorisation of olive oil adulterated by hazelnut oil (Flores *et al.* 2006; Pavón *et al.* 2009). Three groups were recognised within the analysed set of the model samples:

(1) Products free of hazelnuts (filbertone under the detection limit 2 μg/kg) and samples with minimal content of hazelnuts (less than 1%, which corresponds to the filbertone content lower than 4 μg/kg).

(2) Samples with middle contents of hazelnuts (from 1% to 10%, which corresponds to the filbertone content from 4 to 45 μg/kg).

(3) Superior samples with high contents of hazelnuts (above 10%, the filbertone content above 45 μg/kg).

This classification recognised correctly all 30 measured model samples. And only the spread produced from paste E (that with the highest content of filbertone) would be, in calculating the theoretical yield of filbertone, erroneously classified into the superior category (above 10% hazelnut paste), due to its filbertone content above 45 μg/kg.

The proposed model is not sufficiently robust to allow the calculation, with an adequate margin of error, of the hazelnuts content in spreads. However, it allows the grading of the products according to filbertone content into three quality groups and can be used in monitored campaigns organised to evaluate the situation on the market.

Commercial hazelnut spread quality control

To verify if the presence of hazelnuts in relevant products can be proven and graded according to filbertone content, a set containing the real hazelnut spread samples purchased from the market was analysed. The achieved results of filbertone content

Table 2. Specification and filbertone content in commercially available hazelnut spreads and their classification

Sample	Filbertone (μg/kg)	Calculated content of hazelnuts (%)	Final sample evaluation	Declared content of hazelnuts (%)
1	59 ± 5	14	superior sample with a high content of hazelnuts	13
2	70 ± 6	17	superior sample with a high content of hazelnuts	16
3	12 ± 1	3	sample with a middle content of hazelnuts	5
4	80 ± 6	19	superior sample with a high content of hazelnuts	not declared
5	61 ± 5	14	superior sample with a high content of hazelnuts	not declared
6	below quantification limit	traces	sample with a minimal content of hazelnuts	0.01
7	below quantification limit	traces	sample with a minimal content of hazelnuts	0

and subsequent products evaluation according to the proposed methodology are given in Table 2. All analysed hazelnut commercial spreads, claimed to contain particular amounts of hazelnuts, were found to be authentic and fulfilled the requirements of the recent EU legislation. On the other hand, sample No. 7 was found to contain traces of undeclared hazelnuts, which is essential from the point of view of hidden allergen.

Due to the high variability of filbertone content in the hazelnuts and hazelnut products, filbertone cannot be used as a single authenticity marker or for the precise quantification of the hazelnut contents in hazelnut spreads and products. But it allows to estimate the hazelnut content and to evaluate the quality and authenticity of hazelnut spreads.

The conclusions are not valid if the fraudulent synthetic or natural nut-like flavours based on filbertone are used to improve on or mask the product composition. If a synthetic racemate is misused, a significant modification of enantiomeric ratio would be observed by chiral analyses (Castillo *et al.* 2002).

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Corresponding author:

Ing. Jitka Šnebergrová, Vysoká škola chemicko-technologická v Praze. Fakulta potravinářské a biochemické technologie, Ústav konzervace potravin, Technická 5, 166 28 Praha 6, Česká republika; E-mail: jitka.snebergrova@vscht.cz