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Profiling flavor compounds of potato crisps during storage using solid-phase microextraction☆

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Abstract

Headspace solid-phase microextraction (HS-SPME) was studied as a solvent free alternative method for the extraction and characterisation of volatile compounds in stored potato crisps by capillary gas chromatography coupled with mass detection. Better results were obtained when extraction was carried out at 70 °C using a divinylbenzene (DVB)–carboxen (CAR)–polydimethylsiloxane fiber. The fiber was exposed for 20 min (extraction time) to the sample headspace, immediately after an equilibrium time of 5 min (time needed to reach the equilibrium between sample and above headspace). A total of 31 compounds were identified in oxidised potato crisps and resulted mainly from the degradation/rearrangement of lipids and carbohydrates.
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Keywords: Solid-phase microextraction; Volatile organic compounds; Lipid oxidation; Potato crisps; Food analysis

1. Introduction

Consumers' acceptance of foodstuffs is closely related to its flavor. Therefore, it is not surprising the interest on developing newer methods for volatile compounds analysis.

Conventional methods for extraction and pre-concentration of volatiles include: liquid–liquid extraction [1], distillation [2–4], supercritical fluid extraction [5] and solid-phase extraction [6]. These present several disadvantages: are time-consuming, use expensive and hazardous organic solvents, loss analytes during extraction, need sophisticated equipment and require large sample volume [7–9]. Static [10,11] and dynamic headspace [4,12,13] as well as purge and trap [14] methods are fast, simple and solvent free, although presenting the risk of leaks and possible generation of artifacts [15].

In order of overcoming the main drawbacks of these approaches, solid-phase microextraction (SPME) has been developed [8,16]. This sample preparation technique, which enables the simultaneous extraction and pre-concentration steps, has been used, among in other applications, in the study of the volatile profile of foodstuffs [7]. It is very simple, fast, portable, inexpensive and can handle the sample matrix directly [17]. Therefore, it reduces analysis time allowing to process a higher number of samples and avoiding loss of analytes. Furthermore, it presents an important overcome: does not use solvents, which contribute for environmental pollution, health hazard as well as purchase and disposal costs. Due its advantages, SPME has already been applied to a wide range of matrices, like: meat [18,19]; fruits [15,20–22]; truffles [23]; virgen olive oil [24]; cheese [7]; vinegar [9] and alcoholic beverages [25–27].

SPME bases on the adsorption of analytes directly from samples onto a coated fused silica fiber. The extraction of analytes can be performed with the fiber directly immersed in

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the sample (in the liquid state)-direct immersion (DI)-SPME, or otherwise, with the fiber exposed in the vapour phase above a gaseous, liquid or solid sample—headspace SPME (HS-SPME). Using HS-SPME the fiber is not in contact with the sample, increasing, this way, the fiber lifetime. Moreover, HS-SPME is more recommended for highly volatile analytes once the low volatility of larger molecules may decrease the mass transfer from the sample to the headspace, originating a longer extraction time [1,8,17,25].

In the past few years the SPME technique has suffered important advances in order to achieve optimal results. Therefore, today are available several types of coating fibers for compounds extraction which differ on the polarity (chemical nature) and thickness of the stationary phase [8]. The selection of the appropriate fiber should be made in accordance with the properties of the analytes. The amount of compounds extracted depends on the different affinities of the compounds for the fiber and on the competition phenomenon. This way, a non-polar fiber, like polydimethylsiloxane (PDMS), extracts, mainly, non-polar compounds (volatile compounds) while a more polar fiber, such as polyacrylate (PA) presents a strong discrimination towards non-polar analytes, extracting more polar compounds (phenols and alcohols) from matrix [26].

Mixed phases such as carboxen (CAR)–PDMS, carbowax (CW)–divinylbenzene (DVB) and DVB–CAR–PDMS present medium polarity, reducing the discrimination towards very nonpolar and polar volatile compounds. Therefore, they are preferred when a multicomponent analysis is carried out. Many authors have compared fiber coating to select the most appropriated [7,11,20,26,28]. Mixed fibers, which contain carboxen or/and divinylbenzene absorbers presented better results when compared with “single fibers” (PDMS or PA fibers) [8,11,26,29].

Finally, the analytes are thermally desorbed in the GC injector or in a desorption chamber employing the mobile phase, when liquid chromatography is applied, and they are separated on the column. The result is a “fingerprint” chromatogram, where it is possible to determine compounds that are responsible for the off-flavors.

The high oil content of potato crisps, which come from the frying process, provides a great vulnerability to oxidative rancidity, reducing the crisps shelf-life [30].

The present paper reports the development of a SPME sampling method useful for the investigation of volatile compounds released during the storage of potato crisps. Herein, crisps flavor was studied, by means of an accelerated storage test, which is commonly used to obtain information on product stability. The later was performed in order to identify the compounds formed during lipid oxidation process.

2. Experimental

2.1. Sampling and analytical standards

Potato crisps were purchased from a supermarket in Santiago de Compostela (Spain). They contained: 33.2% lipid; 7.2% protein; 14.3% sugar; and less than 1% sodium. After a gas chromatography–mass spectrometry (GC–MS) analysis, they were stored in presence of natural light. Potato crisps brand was selected regarding the type of oil used to fry and the packaging film employed. Selected crisps were fried in olive oil and were packed with a transparent film in order to evaluate the changes in the profile of volatiles substances under accelerated conditions of oxidation. Immediately before analysis, potato crisps were ground using an electronic grinder (Taurus, G70, Lerida, Spain).

Hexanal (CAS 66-25-1), octanal (CAS 124-13-0), decanal (CAS 112-31-2), octanol (CAS 111-87-15) and hexanoic acid (142-62-1) were supplied from Sigma–Aldrich (Madrid, Spain) and had a purity above 99%.

2.2. SPME procedure

The SPME fibres and the manual holder were purchased from Supelco (Bellefonte, PA, USA). The following types of SPME fibres were used: PDMS–DVB with 65 μm thickness; CAR–PDMS with 75 μm thickness; DVB–CAR–PDMS with 50/30 μm thickness. Fibers were conditioned following the manufacturer’s instructions previous to use: PDMS–DVB was inserted 30 min at 260 °C; CAR–PDMS was inserted 30 min at 280 °C while DVB–CAR–PDMS was inserted 4 h at 270 °C.

Approximately 0.1 g of ground sample was placed in a 20 mL clear glass vial (Sun International Trading, USA) and hermetically sealed with a PTFE-coated silicone cap. Vials were heated at 70 °C for 5 min to condition for the equilibrium time. Then, the fiber was introduced into the vial and it was exposed to the sample headspace during 20 min (extraction time). Following sampling, the fiber was retracted and removed from the vial. Fibers were immediately thermal desorpted in the injection port during 3 min at 260 °C in order to prevent possible contamination. Each SPME sampling was conducted in triplicate.

2.3. Gas chromatography–mass spectrometry

GC-MS analysis was performed in a mass selective detector MD 800 coupled to a gas chromatograph Fisons model 8000 (Manchester, UK). The injector port was lined with a 0.8 mm i.d. narrow-bore glass liner (SGE, USA) and maintained at 260 °C. The fused silica capillary column DB-5 (30 m × 0.25 mm i.d., 1 μm film thickness) equivalent to a 5% phenyli–95% methylsiloxane (DB J&W Scientific, CA, USA) was used.

The head pressure of the carrier gas helium (high purity) was 70 kPa. The temperature program was set at an initial 40 °C for 1 min, followed by an increase of 20 °C/min to 120 °C, held for 8 min, then increased to 260 °C at a rate of 20 °C/min and held for 2 min. Purge and bottom valves were closed for 2 min. All analysis were conducted under the same MS conditions. The MS detector was operated in the full scan mode with 70 eV electron ionisation, by scanning a mass

range of m/z 35–300 in 0.45 s. The system was computer-controlled using the Masslab (Version 1.4) software.

2.4. Compounds identification

Components were identified by matching their mass spectra with the Wiley spectral library. Compounds were identified with a resemblance percentage above 85%. Some of the most predominant flavor compounds were further identified by comparison of their retention times with those of pure standard compounds (hexanal, octanal, octanol, decanal and hexanoic acid).

3. Results and discussion

3.1. Method optimisation

A comparison of three mixed fibers: PDMS–DVB (partially crosslinked); CAR–PDMS (partially crosslinked); DVB–CAR–PDMS (highly crosslinked) was conducted to select the optimum fiber coating for the analysis of potato crisps volatiles. The inter-fiber comparison was performed, according Augusto et al. [20], calculating the normalised extraction efficiency N_x. This parameter was defined as $N = 100\,[\Sigma_x/\Sigma_{(\mathrm{DVB\text{–}CAR\text{–}DMS})}]$ where Σ_x is the sum of the areas of the detected peaks of stored potato crisps with the fiber x and $\Sigma_{(\mathrm{DVE\text{–}CAR\text{–}PDMS})}$ is the corresponding sum with DVB–CAR–PDMS fiber.

As expected DVB–CAR–PDMS and PDMS–DVB fibers showed similar extraction efficiency. PDMS/DVB has already been selected for the analysis of volatile compounds from infant milk powder oxidation [30] and for the analysis of volatile compounds of coffee [11] due to its good performance. According to Augusto et al. [20] calculated normalised extraction efficiency for both fibers was the same. When CAR–PDMS was used only 96% extraction efficiency was obtained with respect to the other two fibers. Results were calculated as an average of duplicate extractions and the variation between duplicates was greater for CAR–PDMS fiber (10%), 6% for PDMS–DVB fiber and smaller for DVB–CAR–PDMS (2%). From these results, DVB–CAR–PDMS was selected for profiling volatiles of stored potato crisps.

The adsorption temperature and time were set at 20 min and 70 °C, respectively for all analysis. Samples were heated to enhance the release of analytes into the headspace. However, much attention has to be taken to avoid artifacts once high temperature increase the likelihood of sample alteration with consequent artifactual oxidation [31].

An equilibrium time (time needed to reach the equilibrium between sample and above headspace) of 5 min was set. Selected conditions were optimised in order to avoid fiber and/or detector saturation even for the more concentrated sample (more oxidised potato crisps).

Sample size is critical on the extraction once influences the amount of volatiles compounds extracted. Therefore, distinct quantities of sample were assayed (0.1–0.5 g). A great sample amount produces fiber saturation while a small sample size may yield a considerable RSD. Best results were obtained with 0.1 g sample, when using the 0.5 mm i.d. liner and 1 g sample with the 2 mm i.d. liner.

3.2. Optimisation of desorption conditions

The injection port temperature as well as the desorption time were optimised to ensure that volatiles were totally desorbed from fiber. The optimal results were achieved with a temperature of 260 °C for 3 min. Memory effect of the fiber was excluded with the blank analysis performed after each run. The fibers lifetime used to be approximately of 60 samples. Fiber ageing, which used to originate new peaks, was

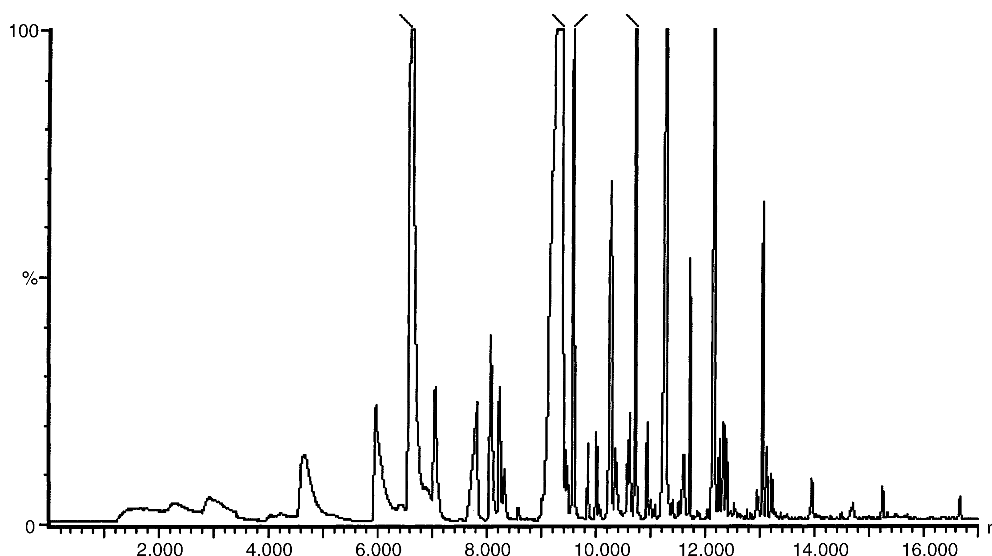

Fig. 1. GC–MS chromatograms of potato crisps flavor after extraction with a 2 mm i.d. liner. rt, retention time in min.

Table 1
Comparison of compounds identified using liners with different internal diameters

Group	Compound	Liner	
		2 mm i.d.	0.8 mm i.d.
Alcohols	3-Methyl, 1-butanol	x	x
	Heptanol	x	x
	1-Octanol	x	x
	1,5-Heptadiene-3,4-diol		x
	1-Nonanol	x	x
Aldehydes	3-Methyl butanal	x	x
	Hexanal	x	x
	Heptanal	x	x
	Octanal	x	x
	Nonanal	x	x
	Decanal	x	x
	trans,*trans*-2,4-Nonadienal		x
	2-Undecenal		x
Carboxilic acids	Acetic acid	x	x
	Propanoic acid		x
	Hexanoic acid	x	x
	Heptanoic acid	x	x
	Octanoic acid	x	x
	2-Octenoic acid		x
	Nonanoic acid	x	x
	Decanoic acid	x	
Esters	Pentyl ester formic acid	x	
	Pentyl ester hexanoic acid	x	x
Furans	Tetrahydro-2-methyl furan		x
	2-Pentylfuran		x
Hydrocarbones	Pentyloxirane	x	
	6-Methyl-1-heptene		x
	Bicyclo-2,2,2-1-methyloctane	x	
Ketones	2-Heptanone	x	x
	3(E), 3-octen-2-one	x	x
	2-Nonanone	x	x
	3-Nonen-2-one	x	x
	2-Decanone	x	x
Others	*trans*-Tetrahydro-5,6-dimethyl-2H-2-pyranone		x
	5-Ethyl-dihydro-2(3)-furanone		x
	5-Pentyl-2(5)-furanone	x	
	5-Hexylhydro-2(3)-furanone	x	
		27	31

controlled with running blank samples. Moreover, fiber position in the GC was also studied, considering that the injector is not uniformly heated [17]. A desorption deep of 3 cm was chosen to perform all experiments. The normal inlet liner (2 mm i.d.) was changed by a narrow (0.8 mm i.d.) liner in order to improve GC resolution.

The internal diameter of the liner has a significant effect on the chromatographic peaks of extracted compounds. Peak broadening effect is remarkably minimized for analytes with low boiling points (b.p.) and almost eliminated for compounds with higher b.p. Fig. 1 shows the chromatogram obtained from an oxidised crisps sample using a 2 mm liner. Table 1 compares the compounds identified in oxidised potato crisps after SPME extraction with two liners of different internal diameters. With the 2 mm i.d. liner, 27 compounds were identified, while using a 0.8 mm i.d. liner, 31 compounds were identified.

The repeatability of the method was determined for the two liners by using six replicate samples of potato crisps stored during the same period of time. Repeatability depends from compound to compound but, in general, using 1 g sample and 2 mm i.d. liner enables lower RSD (average 9%) than 0.1 g sample with a 0.8 mm liner (average 11%). The main reason for this is the small sample size that, as we have already said, yields a considerable RSD.

With the aim of obtaining a good chromatographic resolution from the headspace stored potato crisps, several ramp temperatures were studied. The chosen ramp was chosen once allowed to separate better and therefore identify more volatile compounds released during the storage of potato crisps.

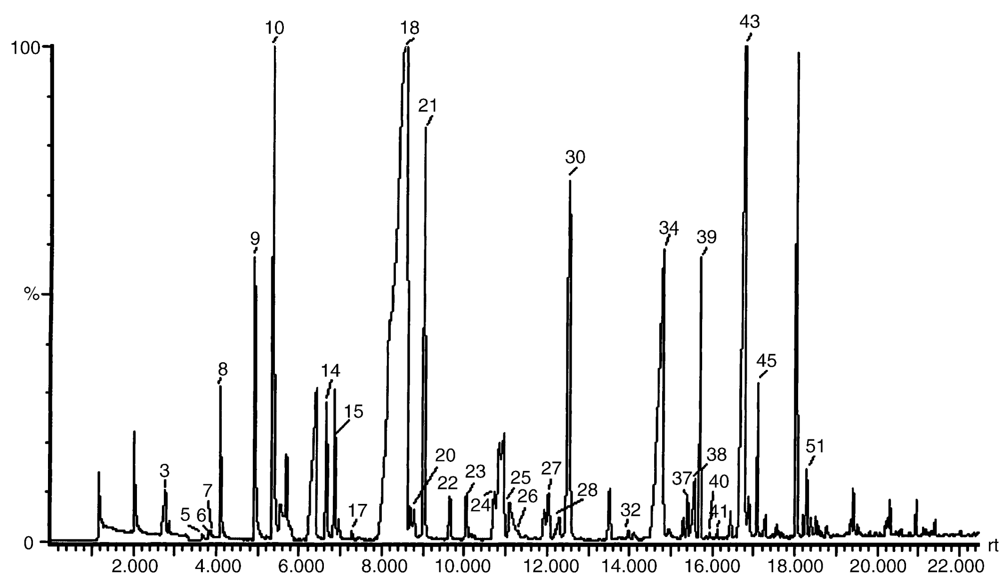

Fig. 2. Total ion current (TIC) mass chromatograms of oxidized potato crisps. rt, retention time in min.

3.3. Volatile compounds formed during crisps storage

A GC–MS analysis was carried out in order to identify the volatile compounds of stored potato crisps. Fig. 2 shows the total ion current (TIC) mass chromatogram of potato crisps after a three-month storage period at room temperature in presence of natural light.

The identified and quantified (%) compounds in oxidised potato crisps are listed in Table 2. The values correspond to the arithmetic mean ± standard deviations of six samples stored in the same conditions. These correspond to the following chemical families: alcohols (1); aldehydes (2); carboxylic acids (3); esters (4); furans (5); hydrocarbons (6); ketones (7); others (8). These compounds accounted for 87.8% of the total integrated peak areas.

A consideration that had to be taken in account was that no peaks appeared in the blank runs, thus indicating that no compounds due to the fiber or contamination were expected.

3.3.1. Aldehydes

The aldehydes group constitute the second most important family of volatile compounds from a quantitative point of view in oxidised potato crisps (19%).

Most of the identified aldehydes presented straight chain such as hexanal, heptanal, octanal, nonanal, decanal, *trans*,*trans*-2,4-nonadienal and 2-undecenal.

These compounds result from a degradative reaction of lipid oxidation of unsaturated fatty acids (oleic, linoleic and linolenic)—autoxidation—which is not enzymatically catalyzed once lipoxygenase and hydroperoxidases are destroyed during thermal processing [32–34]. Indeed, these compounds contribute to the aroma of oxidised crisps due to its low odour threshold [35].

The amount of hexanal, heptanal, octanal and nonanal have increased during storage. Thus, as would be expected, flavor quality have decreased with storage time. Hexanal has been used as indicator of the state of lipid oxidation because it concentration increases during storage and it has a low perception threshold which means hexanal plays an important role in the off-flavors of rancid potato crisps. Hexanal come from linoleic acid via the 13-hydroperoxide. Nevertheless, can also appear later as an autoxidation product of the 2,4-decadienal [18,32].

Besides linear aldehydes, a branched-chain aldehyde was also identified, 3-methylbutanal, which presents a bitter nut, green plant like aroma [32,36]. This compound is derived from the amino acid leucine [37]. It major formation pathway seems to be the oxidative deamination–decarboxylation via Strecker degradation and it has already been identified in green beans [33] specially those pressure cooked once high temperature catalysis its formation reaction [32,36].

3.3.2. Ketones

Five ketones were identified (Table 2), of which there were methylketones. Ketones as well as the others carbonyl compounds have their origin in the oxidative degradation of unsaturated fatty acids [4].

In many fruits and vegetables these compounds are only minor components but act as potential "feed chemical" for reactions which yield volatile flavor compounds. In potato crisps unsaturated fatty acids come, mainly, from the oil used to fry, in this case, olive oil [38]. Ketones are responsible for the flavor of many fruits; vegetables and dairy products like blue cheeses where they are by-products of the fermentation process [35].

3.3.3. Alcohols

A total of five alcohols were identified. Higher-molecular-weight alcohols tend to exist in the liquid form due to the vapour pressure. Therefore, they have minor significance in

the flavor once they present higher odours thresholds [36,39]. Likewise other carbonyl compounds, they are yielded by chemical degradation of hydroperoxides of unsaturated fatty acids and some may result from the reduction of carbonyl compounds [40].

The alcohol, 3-methyl-1-butanol is generated via Strecker degradation. Leucine reacts with 2-ketoglutamic acid (the amino group acceptor) in a reaction catalysed by L-leucine amino transferase [33].

3.3.4. Carboxylic acids

Carboxilic acids was the most important class of compounds identified in potato crisps submitted to analysis after a three month storage. They constituted 65.35% of total peaks area. The most abundant compound in the volatile fraction was hexanoic acid (38.36%) (Fig. 3).

Most of them are final products of lipid oxidation reactions, which result from the decomposition of products of fat or by deamination of amino acids [40], therefore they indicate that the analysed potato crisps presented an advanced lipid oxidation state. In general they present fruity, painty, acid and green-like aroma. Coleman et al. [40] have reported the identification of acetic, propanoic, hexanoic and heptanoic acids in baked potato flavor.

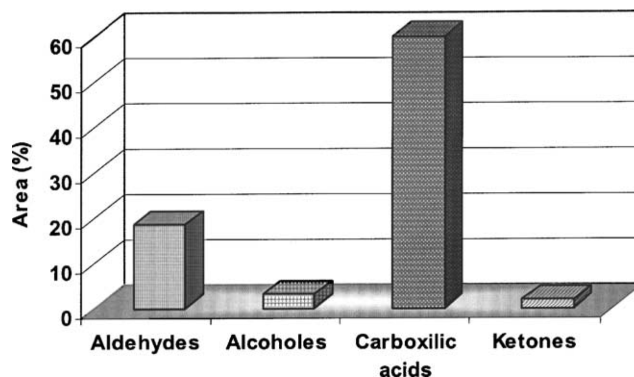

Fig. 3. Profiles (% area) of the major volatile families of oxidized potato crisps.

3.3.5. Esters

Esters result from the esterification of carboxylic acids and alcohols [35]. Esters, mainly the short chain acids, are responsible for fruity aromas [33]. Therefore, they have been found in olive oil [41]. In stored crisps just pentyl hexanoate was identified with the 0.8 mm liner.

3.3.6. Furans

Two furans (2-methyltetrahydrofuran and 2-pentylfuran) with a green and fruity aroma have been identified in oxidised

Table 2
Compounds identified and quantified (%) in oxidized potato crisps after SPME extraction

Peak no.	Compound name	t_R (min)	Type	Oxidised potato crisps (% area ± SD)
3	Acetic acid	2.79	4	0.391 ± 0.084
5	*trans*-Tetrahydro-5,6-dimethyl-2H-2-pyranone	3.68	8	0.063 ± 0.010
6	Tetrariydro-2-methyl furan	3.83	5	0.055 ± 0.009
7	Propanoic acid	3.90	4	0.069 ± 0.015
8	3-Methyrbutanal	4.11	1	0.966 ± 0.152
9	3-Methyl, 1-butanol	4.94	3	1.524 ± 0.126
10	Hexanal	5.39	1	6.220 ± 0.525
14	2-Heptanone	6.68	2	0.857 ± 0.082
15	Heptanal	6.88	1	0.960 ± 0.078
17	1-Heptene-6-methyl	7.31	6	0.060 ± 0.007
18	Hexanoic acid	8.77	4	38.365 ± 1.557
20	2-Pentyl furan	8.82	5	0.192 ± 0.046
21	Octanal	9.07	1	3.567 ± 0.137
22	Heptanol	9.70	3	0.400 ± 0.032
2	3(*E*),3-Octen-2-one	10.11	2	0.436 ± 0.038
24	5-Ethyldihydro-2(3)-furanone	10.78	8	0.531 ± 0.107
25	Heptanoic acid	11.11	4	3.979 ± 0.660
26	1-Octanol	11.30	3	0.771 ± 0.084
27	2-Nonanone	12.01	2	0.369 ± 0.016
28	1,5-Heptadiene-3,4-diol	12.10	3	0.531 ± 0.055
30	Nonanal	12.60	1	4.998 ± 0.147
32	3-Nonen-2-one	14.03	2	0.094 ± 0.008
34	Octanoic acid	14.90	4	8.848 ± 0.506
37	2-Decanone	15.44	2	0.268 ± 0.027
38	2-Octenoic acid	15.64	4	0.756 ± 0.069
39	Decanal	15.74	1	1.849 ± 0.062
40	*trans*,*trans*-Nona-2,4-dienal	15.97	1	0.032 ± 0.005
41	1-Nonanol	16.15	3	0.052 ± 0.005
43	Nonanoic acid	16.84	4	9.778 ± 0.864
45	Pentyl ester hexanoic acid	17.12	7	0.778 ± 0.041
51	2-Undecenal	18.23	1	0.113 ± 0.021

potato crisps. 2-Pentylfuran has already been identified in baked potatoes [40].

3.3.7. Other compounds

Other compounds identified (1 hydrocarbon-6-methyl-l-heptene-, 1 furanone and 1 pyranone) present minor importance to crisps flavor.

4. Conclusions

The HS-SPME procedure is a non-evasive, solvent-free method presenting major advantages: simplicity, rapidity, high sensitivity and small sample volume.

The HS-SPME method is appropriated for the volatile profile study of potato crisps. It allowed the identification of 31 compounds, most of them resulted from degradation/rearrangement of lipids and carbohydrates and have grassy notes.

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