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On-line dynamic HS-SPME for monitoring endogenous aroma compounds released during the baking of a model cake

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ABSTRACT

This work shows that using a dynamic SPME device combined with an instrumented oven, it is possible to monitor the release of a large amount of volatile compounds generated during the baking process of a real cereal product (sponge cake model) by directly sampling its baking vapours. The steam assisted dynamic SPME device made it possible to extract volatile compounds with very different volatility and hydrophobicity, such as 5-hydroxymethylfurfural and 2-methyl-propanal. Time dependent analyses of baking vapours made it possible to simultaneously follow the release of several odour compounds and thermal reaction markers at different stages of their generation in the sponge cake model. The release of newly formed aroma compounds during baking significantly affected the odour quality of baking extracts as shown by odour profiles and sensory preferences evaluated by Direct-GC–Olfactometry. GC–Olfactometry analysis was carried out on the final baking fractions to gain an understanding of the compounds which could contribute to overall odour quality.

1. Introduction

During a thermal process such as baking, food products undergo intense transformation due to heat and mass transfer. Such changes are also partially governed by the initial composition of food ingredients which constitute the medium of the reactions (Chevalier, Colonna, Valle, & Lourdin, 2000). The baking of cereal products leads to a huge quantity of newly formed volatile compounds which play a major role in developing the flavour of the final product. These compounds are mainly the result of the Maillard reaction which occurs between reducing sugars and the -NH_2 function of amino acids, peptides and proteins (Baltes, 1982). However, depending on raw material composition and processes, the Maillard reaction is not necessarily the only thermal reaction occurring during baking. In fact, both caramelisation and lipid oxidation can also take place. These reactions are known to be involved in the generation of odour active compounds such as aliphatic aldehydes and furfurals (Grosch & Schieberle, 1997; Kroh, 1994; Whitfield, 1992).

Over the past few years numerous studies have dealt with the identification and quantification of the molecular compounds which have an impact on the flavour of the most common cereal products such as bread (Schieberle & Grosch, 1985; Schieberle & Grosch, 1992), the French baguette (Zehentbauer & Grosch, 1998), and cookies (Prost, Lee, Giampaoli, & Richard, 1993). The goal of such work has been to gain a deeper understanding of the role played by fermentation, enzyme activity and food components such as sugars and fat. Pozo-Bayon, Ruiz-Rodriguez, Pernin, and Cayot, (2007) recently showed that changing the formula of a sponge cake by substituting eggs with a leavening agent, produced important changes in some key aroma compounds such as methional. Few interesting studies have been made on the impact of specific thermal processes, such as extrusion, on the generation of flavour compounds and its sensory impact (Heiniö et al., 2003). An extensive work about baked cereal products reviews bibliographic data about aroma generation and summarises the possible elaboration methods that can be used to control or modify flavour in this type of product (Pozo-Bayón, Guichard, & Cayot 2006a, 2006b). However, it has recently been pointed out that in addition to having a strong impact on organoleptic quality (i.e. colour and flavour development) some thermally driven reactions can have an effect on nutritive value, produce antioxidative components and have toxicological implications. These findings explain why numerous research groups are today involved in research projects aimed at gaining increased understanding of the reaction mechanisms occurring in food and determining "global" food quality (Cost action 927; Martins, Jongen, & van Boekel, 2001; van Boekel, 2006).

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Moreover, it now appears necessary to have multi-compounds and dynamic methods to follow not only flavour compounds but also some sensitive reaction products (i.e. furanic compounds). For cereal products, the amount of aroma compounds and/or of some volatile Maillard Reaction Products (MRP) is classically measured in the final food by extracting molecules by solvent extraction (Ramirez-Jimenez, Garcia-Villanova, & Guerra-Hernandez, 2000) or using headspace techniques (Poinot et al., 2007; Pozo-Bayón, Guichard & Cayot, 2006a; Pozo-Bayón, Guichard & Cayot, 2006b). These approaches are useful for evaluating the impact of such compounds on food quality but give no kinetic information. It is, in fact, worth stressing that many chemical and physical parameters (i.e. Aw, concentration of reactants, pH, etc.) are simultaneously changed during thermal processing of food, thus affecting the generation of aroma compounds. A novel approach to treating this problem is to monitor volatile compounds (flavour or interesting reaction markers) during their development, that is to say during the thermal process. From an analytical point of view, an interesting dynamic approach has been applied to a roast-beef model by Rochat and Chantreau, (2005). Using headspace trapping and GC–Olfactometry, the authors analysed molecular compounds generated during the baking of roast-beef which affected the odour of the in-oven roast-beef top note. A similar approach was adopted by Rega, Guerard, Maire, and Giampaoli (2006) who showed that using an on-line dynamic SPME device combined with an instrumented oven it was possible to sample volatile compounds released throughout the baking of a model sponge cake. The authors also used Direct-GC–Olfactometry (D-GC–O) to assess the odour representativeness of dynamic SPME extracts of baking aroma obtained by different SPME fibres.

The aim of the present work was to investigate the release of the endogenous volatile compounds formed during the baking process of a model sponge cake and specifically examine whether by monitoring baking vapours during the thermal process information could be obtained about their evolution. Volatile compounds with interesting flavour characteristics and/or which are good thermal reaction markers were followed in the vapours generated at different stages of baking using an on-line steam assisted dynamic SPME device. Both sensory and instrumental analyses were carried out to identify the fraction of baking generating the best sensory appreciation and then to identify the corresponding odour active compounds. The volatile compound composition was also followed in the cake matrices. In future developments, such a dynamic approach could help to gain an understanding of the reaction pathways and kinetics occurring in a real food system during physical and chemical thermal transformation.

2. Experimental

2.1. Sponge cake making

The sponge cake formula was composed of with 60 g flour (moisture content 13% w/w), 60 g sucrose (0.4 mm diameter), 9.6 g palm oil, 1.2 g sodium chloride, and 109 g pasteurised liquid eggs (76% w/w moisture content), all purchased in a local market. The ingredients and procedure were established following Pozo-Bayón et al. (2006a); Pozo-Bayón, Guichard, and Cayot (2006b).

2.2. Dough preparation

The liquid eggs, sucrose, and salt were mixed together using a household mixer (Moulinex, max speed) in a water bath at 50 °C (±2 °C) for 5 min. The mixture was removed from the water bath and, after being left to set 1 min at room temperature, was mixed again for 2 min. The flour was then progressively added and gently incorporated into the foam. Melted palm oil (50 °C) was then slowly added to the mixture.

2.3. Baking

Two hundred and ten grams of dough were immediately poured into a cake mould (25 cm × 6 cm × 10 cm) and baked at 170 °C (±10 °C) for 25 min in a convection oven (Scholtès) specifically instrumented for the collection of baking vapours under controlled temperature conditions. During baking, the temperatures of the oven and at the cake core (T_{core}) were measured by a *K*-type thermocouple connected to a Pico 8-channel Thermocouple Data Loger. A mean weigh loss of 13 ± 0.5% (humid weigh) was observed after 25 min baking.

2.4. On-line SPME extraction and analysis of vapours during baking

A modified method for dynamic SPME sampling was adapted to baking vapours from previous work on strawberry yoghurt headspace (Delarue, Chanlot, Richard, & Giampaoli, 2003). During the baking of the sponge cake, the hot vapours generated were continuously carried through a glass inlet hood to a refrigerated extraction chamber (pyrex, cone geometry, $V = 40$ mL, $T = 5 \pm 2$ °C) at a constant flow rate of 7.5 L/min using a membrane pump (Ilmvac, France) equipped with a flow regulation valve. As they passed through the extraction chamber, the vapours were continuously sampled by an SPME fibre. Preliminary experiments on colour, water content and morphology of the model cake showed that this sampling mode provoked no perturbation of the cooking (data not shown). Temperatures of both the oven and the extraction chamber were monitored by means of two *K*-type thermocouples connected to a Pico 8-channel Thermocouple Data Loger. SPME extractions of volatile compounds were performed dynamically in two ways: *-1-* throughout baking (25 min) and *-2-* at different baking intervals (0–5 min, 5–15 min, and 15–25 min). Three different SPME fibres were tested for their different selectivities: 100 μm PDMS, 75 μm CAR/PDMS and Stableflex 50/30 μm DVB/Car/PDMS (Supelco Bellfonte, PA). These fibres were also chosen for their ability to give SPME extract with a global odour close to that of a baking sponge cake, as shown in a previous paper (Rega et al., 2006). Before each extraction, blanks of both fibre and oven backgrounds were systematically made in order to avoid any eventual parasite signal. Moreover, oven pirolysis (4 h at 350 °C) was carried out daily before analysis. All samples were immediately analysed in triplicate by GC–MS.

Compound analysis and identification. SPME fibres were desorbed into an HP 6890 gas chromatograph equipped with an MSD 5973 mass detector (Agilent Technologies, Palo Alto, CA, USA). Operating conditions were as follows: DB-Wax column (J&W Science, i.d. 0.32 mm, 30 m, film thickness = 0.5 μm) was held at 40 °C for 5 min, then increased at 5 °C min^{-1} to 240 °C. Helium was used as carrier gas at a linear velocity of 40 cm s^{-1}. The source was kept at 200 °C. The transfer line and the detector were maintained at 250 °C. Mass spectra in the electron impact (EI) mode were generated at 70 eV and collected from m/z 29 to 350, at 3.45 scans s^{-1}. Compounds were identified with standard mass spectra (when available), by comparison with mass spectra libraries (NIST-Gaithersburg MD, INRAMASS-INRA France) and by comparison of Linear Retention Indices measured with two different Column phases (DB-Wax and DB5). In order to confirm identifications, a complementary off-line analysis was performed on the DVB/CAR/PDMS global extract (0–25 min baking) by using GC-GC/TOF LECO PEGASUS III 4 D. Operating conditions were as follows: VF-5 ms first dimension column (30 m, i.d. 250 μm, film thickness 0.25 μm) was held at 40 °C for 5 min, then increased at 5 °C min^{-1} to 240 °C; VF-17 Ms second dimension column (1,79 m, i.d 100 μm,

film thickness 0.20 μm) was held at 50 °C for 5 min then increased at 5 °C/min^{-1} to 250 °C; modulator Quad jet: +25 °C offset; modulation period 10 s; hot pulse 0.6 s; cold pulse 4.40 s; mass range: 33 to 400 *m*/*z* at 100 sp/s, data analysis by LECO ChromaTOF version 2.2. Criteria of identification are also reported in Table 1.

2.5. Sensory evaluation of on-line SPME extracts

2.5.1. Hedonic test and odour description on baking fractions

As our goal was to identify the fraction with the most pleasant odour and to avoid any carryover effect in sensory assessments, it

Table 1
Volatile compounds extracted from baking vapours by on-line dynamic SPME. The main odorants were detected by GC–O analysis on the 15–25 min on-line SPME extract

LRI-exp[a]		LRI-ref[b]		Compounds	Identification[c]	Car/PDMS	PDMS	DVB/Car/PDI	Odour assessement[d] (DVB/Car/PDMS)	
DBwax	DB5	DBwax	DB5						Descriptors	Frequency of detection (n/7)
795	547	821	552	2-Methylpropanal	B,C	X				
920	643	912	641	2-Methylbutanal	B	X		X		
925	646	943	650	3-Methylbutanal	B,C	X	X	X	Chocolate	4
947	703	958	711	2-Pentanone	B,C	X		X		
1046	689	1036	711	2,3-Pentandione	B,C	X	X	X		
1065	797	1065	779	Hexanal	A,B,C	X		X		
1168	905	1172	900	Heptanal	A,B,C	X		X		
1215	991	1212	993	2-Pentylfuran	A,B,C	X		X		
1240	768	1222	766	Pentanol	A,B,C	X		X		
1249	822	1250	828	2-Methylpyrazine	A,B,C	X		X		
1272	1000	1276	1004	Octanal	A,B,C	X	X	X	Citrus/floral	6
1279		1268		1-Hydroxy-2-propanone	B,C	X		X		
1305	903	1303	905	2,5-Dimethylpyrazine	A,B,C	X	X	X	Parfumed rice/cake/crust[e]	7
1312	913	1308	913	2,6-Dimethylpyrazine	A,B,C			X	Parfumed rice/cake/crust[e]	7
1329	917	1321	919	2,3-Dimethylpyrazine	B,C	X		X	Parfumed rice/cake/crust[e]	7
1377	1107	1373	1104	Nonanal	A,B,C	X		X		
1389	1005	1387	1000	2,3,5-Trimethylpyrazine	B,C	X	X	X	Potatoes/earthy	3
1410	1060	1408	1060	(E)-2-octenal	A,B,C	X		X	Unpleasant	4
1432	977	1410	980	1-octen-3-ol	A,B,C	X		X	Mushroom/musty	4
1440	679	1450	660	Acetic acid	A,B,C	X	X	X	Unpleasant/earthy	4
1450	851	1455	852	Furfural	A,B,C	X		X	Cake/crust	
1482	1207	1478	1204	Decanal	A,B,C	X		X	Floral/fruity	4
1500	963	1492	962	Benzaldehyde	A,B,C	X		X		
1517	1168	1509	1160	(E)-2-Nonenal	A,B,C			X	Floral/vegetal/musty	4
1542	1087	1535	1075	Octanol	A,B,C	X		X		
1583	1324	1583	1306	Undecanal	A,B,C	X		X	Floral/bud	4
1605		1605	1023	Acetylpyrazine	A,B,C	X		X	Hazelnut/praline/cake	7
1619	1047	1613	1049	Phenylacetaldehyde	A,B,C	X		X	Leave/rose/floral	3
1620		1588	820	Butyric acid	A,B,C	X		X		
1638	851	1616	863	Furfuryl alcohol	A,B,C	X		X		
1643		1636	1175	Nonanol	A,B,C	X		X		
1693	1412	1682	1412	Dodecanal	A,B,C	X		X	Vegetal/floral	
1804	1368	1793	1366	2-Undecenal	A,B,C	X	X	X		
1811	1297	1775	1309	(E,Z)-2,4-Decadienal	A,B,C	X		X	Fried oil/cooked	5
1838	1321	1805	1318	(E,E)-2,4-Decadienal	A,B,C	X		X	Fried oil/cooked	6
1853		1826	970	Hexanoicacid	B,C	X		X		
1884		1833	925	Dimethylsulfone	B,C	X		X		
1950		1971	1045	2-Acetylpyrrole	B,C	X		X		
1955	1108	1975	1087	2-Methyl-3-hydroxy-4(H)-pyran-4-one (maltol)	A,B,C	X		X		
2061		2006	1700	Pentadecan-2-one	B,C			X		
2066	1077	2043	1090	2,5-Dimethyl-4-hydroxy-(2H)-furan-3-one (furaneol)	A,B,C	X	X	X	Caramel/spice/cake	5
2115		2083	1179	Octanoic acid	A,B,C	X		X		
2168		2177	2116	Tetradecanol	A,B,C		X	X		
2179		2202	1276	Nonanoicacid	A,B,C	X		X		
2244	1161	2274		2,3-Dihydro-3,5-dihydroxy-6-methyl-4(H)-Pyran-4-one	A,B,C	X	X	X		
2461	1251	2410		5-Hydroxymethylfurfural	A,B,C	X	X	X		

[a] Linear Retention Indices on DB-Wax column calculated by injecting a series of alkanes between C_8 and C_{26}.
[b] Linear Retention Index from literature using C20M- and a DB5- type phases (Kondjoyan and Berdagué -1996-, and Flavornet-T. Acree, 2004-data bases).
[c] The identification proposal is indicated as follows: A, compounds identified by MS and LRI as compared with standard injected in the same conditions (all aroma compounds purchased by Sigma–Aldrich) or with those published in literature; B, tentative identification by MS (GC/MS with a quadrupole detection). C, complementary analysis by GC–GC–TOF on the DVB/Car/PDMS extract.
[d] Odour assessement by GC–Olfactometry (four assessors, two repetitions). Only odours associated with an identified compound and detected more than three times are reported.
[e] No discrimination possible due to one broad odour zone from 1300 to 1335 LRI.

was necessary to identify the baking interval corresponding to the release of aroma compounds with a high impact on global odour. We therefore chose to use a hedonic test. Thirty eight panellists were asked to rank the odour of the SPME extracts obtained at different cooking times by the DVB/CAR/PDMS fibre according to personal preference. In order to deliver the global odours of SPME extracts to the panellists, the Direct-GC–Olfactometry tool was used following Rega, Fournier, and Guichard, (2003). This technique is commonly used in the sensory assessment of global odour of solventless extracts (Jouquand & Giampaoli, 2000; Landy, Nicklaus, Semon, Mielle, & Guichard, 2004). An HP 5890 equipped with a sniffing port and a 0.75 mm injector liner was supplied with a short capillary of untreated silica (80 cm × 0.32 mm i.d.). The flow rate of the carrier gas (He) was 25 mL min^{-1} and the oven temperature was kept at 100 °C. SPME extracts were sequentially introduced into the GC port (splitless mode, T = 240 °C) and the resulting odour was evaluated by the assessors. Because no chromatographic separation was carried out by the short silica capillary, aroma compounds arrived rapidly and simultaneously at the sniffing port. Here, for each SPME extract, the assessors perceived and evaluated the resulting global odours. This test is very rapid (about 10 s for each extract, less than 3 min for the whole test). Sensory analysis sessions were performed only after suitable training with the D-GC–O device. Preliminary sensory tests were carried out in order to evaluate the intensity of each SPME baking extract. In order to obtain approximately iso-intense odours, the 0–5 min extract was discharged because it was practically odourless and the SPME extracts of smaller time intervals of baking were chosen: 5–10 min, 10–15 min, 15–20 min and 20–25 min. Samples (odours from SPME extracts) were presented according to a Latin square design. Systematic control was run daily on the chromatographic and odour backgrounds of the SPME fibres and their performance of extraction was periodically controlled. The panellists were asked to rank samples according to preference and also invited to give a free semantic description. Page test was performed on the rankings ($p < 0.05$, XLStat v5.5).

2.5.2. GC–Olfactometry

In order to identify the most odour active molecules, a Gas Chromatography–Olfactometry analysis was run on the final baking fraction (15–25 min). A panel of four trained assessors evaluated the on-line SPME extracts using a Perkin Elmer AutoSystem XL equipped with a flame ionisation detector (FID, 250 °C) and a sniffing port (250 °C). The column (DB-WAX) and chromatographic conditions were the same as described earlier but the GC effluent was split 1:1 between the FID detector and the sniffing port and enriched with purified, humidified air (100 ml min^{-1}). Samples were analysed in duplicate. For each odour stimulus, the panellists recorded the detection time and gave free semantic description. Analyses were carried out in duplicate by all assessors but one, for a total of 7 GC–O analyses. Frequency of detection was performed according to Charles et al. (2000).

2.6. Volatile compound composition of sponge cake

In order to follow the evolution of aroma compounds in the food matrix, a static headspace-SPME (HS-SPME) extraction of volatile compounds was carried out on cakes baked for different baking times using a Stableflex 50/30 μm DVB/CAR/PDMS SPME fibre (Supelco, Bellfonte, PA). The cakes were baked for 5, 15, and 25 min then rapidly cooled under controlled conditions. The per cent of moisture content of the samples was determined by weighing before and after complete desiccation (24 h in an oven at 103 °C) and were 33.5 ± 0.3%, 28.3 ± 1.5% and 24.7 ± 2% after 5, 15, and 25 min baking, respectively.

Five grams of each sample were poured into a 20 mL glass vial (Supelco, Belfonte), and immediately analysed in triplicate. The HS-SPME extraction was automatically performed at 50 °C for 30 min by a Combipal System (Gerstel, Germany) coupled to a HP 6890 gas chromatograph equipped with MSD detector (Agilent Technologies, Palo Alto, CA, USA) in order to minimise further reactions. Operating conditions and identifications were the same as those mentioned above.

3. Results and discussion

3.1. Analysis of global extracts of vapours thoroughout the baking process

In our work, as on-line SPME extraction was carried out under no-equilibrium conditions, the flow rate and the extraction temperature applied to the vapours were crucial parameters for improving extraction recovery and repeatability. Preliminary experiments showed that these two parameters were strictly related so an optimum had to be found for every type of SPME fibre. As an example for the DVB/Car/PDMS fibre, using the actual geometry of the extraction chamber, a high flow rate (7.5 L/min) and an initial chamber temperature of 5 ± 2 °C gave the best results in terms of repeatability, number and range of volatility of the extracted molecules. The temperature of extracting chamber increased rapidly during sampling due to the hot steam flow and reached a plateau at 39 ± 5 °C after 15 min of baking/extraction. This approach with the use of three different SPME coatings, made it possible to extract more than 40 volatile compounds in a broad range of physicochemical properties (Table 1), even very hydrophilic ones like 5-hydroxymethylfurfural (*HMF*) which is very poorly extracted by common headspace and SPME methodologies. Table 1 shows that DVB/CAR/PDMS fibre led to the highest number of extracted compounds and CAR/PDMS fibre made it possible to extract very volatile compounds such as 2-methylpropanal. On the other hand, PDMS fibre proved much less effective than the other solid phases and more sensitive to the oven background. These results are coherent with a previous study on sensory properties of on-line SPME extracts of baking vapours where DVB/CAR/PDMS fibre gave the best sensory results in terms of odour similarity to the reference (the odour of baking cake), despite PDMS extract (Rega et al., 2006) and corroborate those of Poinot et al., (2007) which showed that CAR/PDMS and CAR/PDMS/DVB fibres could obtain odorant extracts representative of bread odour. As shown in Table 1, extracted compounds belong to different chemical classes and could come either from different reaction pathways occurring during baking or from raw materials. 2-Methylpropanal, 2-methylbutanal, and 3-methylbutanal are Strecker's aldehydes coming from valine, isoleucine, and leucine, respectively (Cremer & Eichner, 2000). These aldehydes are very volatile compounds and are well known to be odour active compounds responsible for malty/chocolate notes (Beal & Mottram, 1994). Likewise, phenylacetaldehyde comes from phenylalanine and is responsible for a honey/rose odour (Hofmann & Schieberle, 2000). These compounds may be formed from ingredient precursors during the thermal process. Moreover some volatile compounds coming from lipid degradation pathways were observed. Such was the case of some aliphatic aldehydes such as nonanal and (*E,Z*)-2,4-decadienal, some alcohols like 1-octen-3-ol, and 2-pentylfuran which has already been found amongst the degradation products of linoleic acid and is responsible for "fatty", "fruity" odours (Neff, Warner, & Byrdwell, 2000; Whitfield, 1992). Amongst the extracted heterocyclic compounds, a large number of pyrazines were identified. These

compounds classically belong to "Maillard aroma compounds" and are well known key odorants in cereal products. Most of the extracted compounds were also found by Pozo-Bayon et al. (2007) in baked sponge cake submitted to extensive SAFE and/or Purge and Trap extraction. However, as previously said, dynamic steam assisted SPME conditions made it possible to extract highly hydrophilic compounds not previously observed, such as 2,3-dihydro-3,6-dihydroxy-8-methyl-4H-pyran-4-one (*P*), the most abundant compound in the DVB/Car/PDMS extract. This compound is a Maillard reaction product and a precursor of maltol. Moreover, it is the typical marker of the 2,3-enolization pathway in the Maillard reaction, whereas HMF is the typical marker of 1,2-enolisation (Davidek, Clety, Devaud, Robert, & Blank, 2003). Due to their high hydrophilic character, *HMF* and *P* are classically extracted from bakery products or from model solutions by polar solvents and then analysed by HPLC (Ait Ameur, Trystram, & Birlouez-Aragon, 2006; Davidek et al., 2003; Ramirez-Jimenez, Guerra-Hernandez, & Garcia-Villanova, 2000). Nevertheless, in the present study suitable SPME conditions combined with on-line steam entrainment led to high recovery of these newly formed compounds during the baking process.

3.2. Dynamic monitoring during baking

These compounds represent interesting aroma and/or molecular markers to follow during the baking process of cereal products. As an example, the generation of some interesting volatile compounds was monitored by on-line dynamic SPME during three different stages of baking, namely in the first 5 min of baking, from 5 to 15 min, and from 15 to 25 min. During these three baking stages, oven temperature was constant throughout the baking time (170° ± 10 °C), whereas the temperature of the cake core (T_{core}) was 65.2 ± 7.6 °C, 96.2 ± 0.7 °C, and 95.2 ± 1.7 °C and the temperature of the SPME extraction chamber (T_{extr}) was 13.7 ± 4.2 °C, 31.9 ± 1.3 °C and 39.3 ± 4.9 °C, respectively. Such a global approach takes into account that the amount of compounds extracted by the on-line disposal depends not only on compound concentration in food but also on compound volatility and affinity for the SPME solid phase. It should also be remembered that these are no-equilibrium measurements since concentration, humidity and temperature of baking vapours change during sampling due to dough transformation.

3.2.1. Effect of SPME phase

Fig. 1 shows the formation and release of 2,5-dimethylpyrazine (*DMP*) monitored during baking by three different SPME phases. Due to their different coatings, the SPME fibres extracted different amounts of the compound. The curve slopes are therefore different but a similar (linear) trend is observed depending on the gradual increase of *DMP* with baking time. The same is true for all the other volatile compounds extracted by DVB/Car/PDMS and Car/PDMS polymers. Fig. 1 shows that the PDMS absorbent did not efficiently extract the pyrazine under the applied experimental conditions. Moreover, by comparing relative amounts and standard deviations, very early eluting compounds and pyrazines were better extracted by Car/PDMS adsorbent, whereas most hydrophilic compounds like furanic and pyranic derivatives were better monitored using DVB/Car/PDMS.

3.2.2. Aroma generation and release in baking vapours

The generation and release of volatile compounds during baking is detailed in Figs. 2 and 3 for different groups of molecules according to their chemical origin. Lipid degradation related compounds increased slightly during cooking (Fig. 2). Aliphatic aldehydes and 1-octanol were already present in relatively high amounts at the beginning of baking (up to 5 min), probably because of the early degradation of lipids in food ingredients. This hypothesis has been confirmed by Pozo-Bayon et al., (2007) who found such molecules in the volatile fraction of sponge cake dough before baking. Maillard reaction related compounds are shown in Fig. 3. Strecker's aldehydes and pyrazines (Fig. 3A and B, respectively) followed the same (linear) trend, being completely absent in vapours at the beginning of baking and then gradually increasing. Amongst them 2,5-dimethylpyrazine and 3-methylbutanal were found in relatively high amounts. A completely different trend was shown for *HMF* which was formed and released mainly at the end of the baking process, following an exponential trend (Fig. 3C and D). This result is coherent with that previously shown by Ait Ameur et al., (2006) in model cookies. These authors pointed out that such a compound exponentially accumulated in the food matrix during baking. Similarly to HMF, *P* strongly increased with baking time but following a power law (3d). Its relative amount was however largely predominating on *HMF* after 25 min baking. *P* and *HMF* both have strongly hydrophilic characters (−0.145 and −0.892 log*P* values, respectively) and come respectively from 2,3- and 1,2-enolization of Amadori compound. This result is very

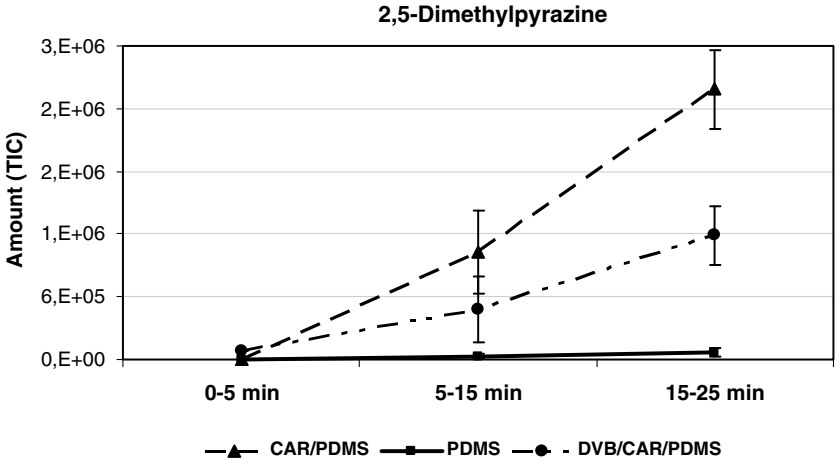

Fig. 1. Release of 2,5-Dimethylpyrazine during three baking intervals (0–5 min, 5–15 min, and 15–25 min) monitored by dynamic on-line SPME using Car/PDMS, PDMS, and DVB/Car/PDMS SPME fibres.

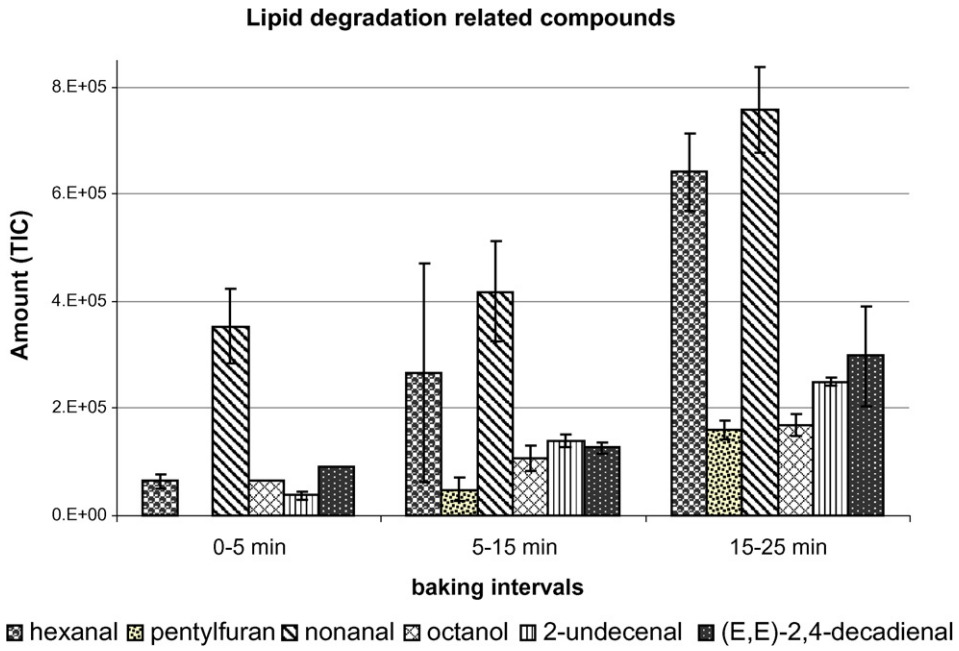

Fig. 2. Release of lipid degradation related compounds during sponge cake baking. Compounds are extracted by dynamic on-line SPME during three baking intervals (0–5 min, 5–15 min, and 15–25 min), using DVB/Car/PDMS fibre.

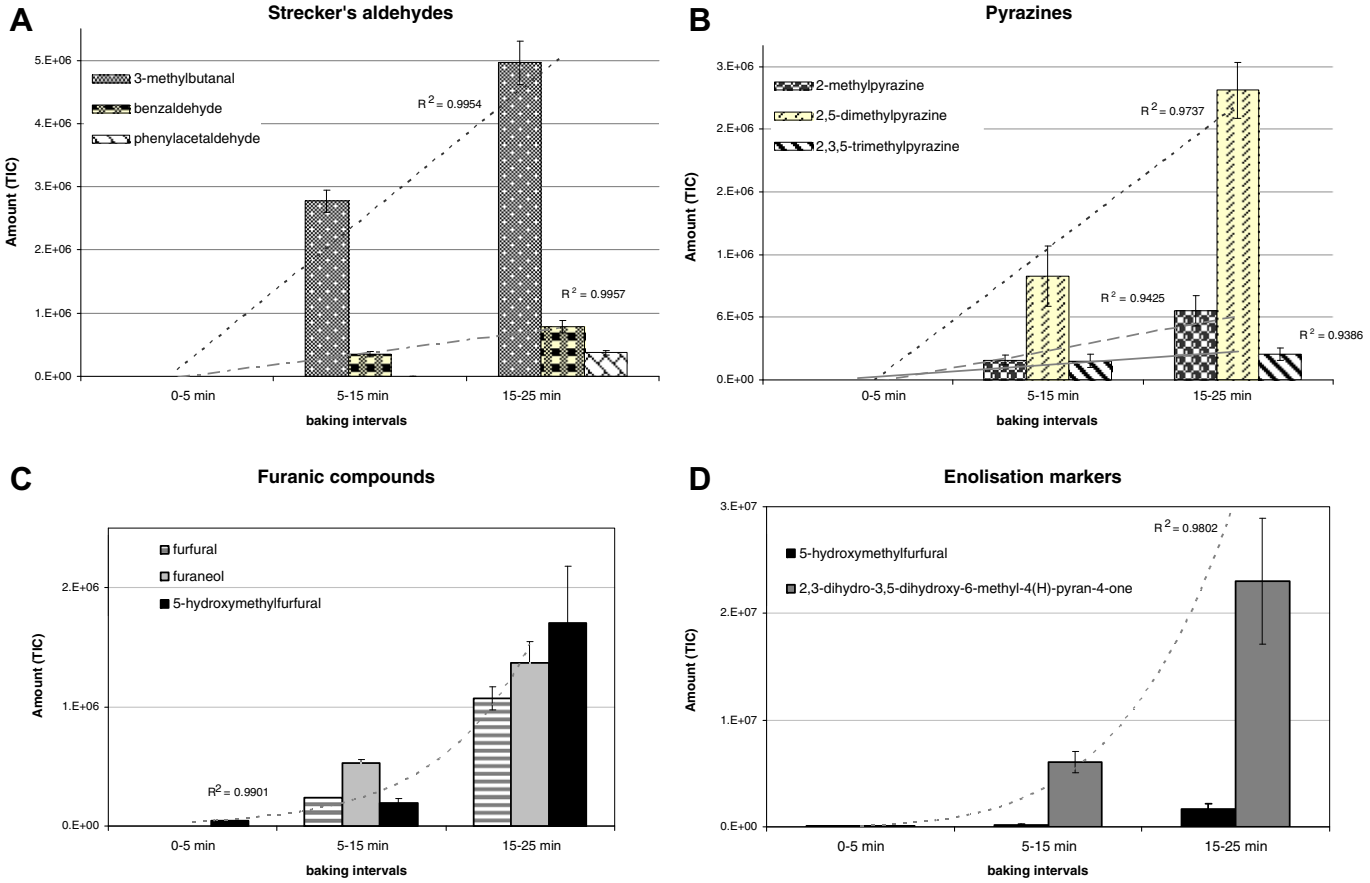

Fig. 3. Release of Maillard reaction related compounds during sponge cake baking. Compounds are extracted by dynamic on-line SPME during three baking intervals (0–5 min, 5–15 min, and 15–25 min), using DVB/Car/PDMS (3A and 3B) and Car/PDMS (3 C and 3D) SPME fibres.

interesting because it shows that thanks to such dynamic on-line extraction it is possible to follow the release of very polar reaction markers which could contribute to the understanding of reaction mechanisms occurring during the baking process.

3.2.3. Sensory evaluation

The hedonic test on odours of SPME baking extracts shows that the evolution of chemical composition during baking significantly affects the odour quality of baking extracts as preference increased with baking times (Page's test on ranking significant at 5%). In particular, the 15–20 min SPME extract was the most highly preferred by the panellists (rank = 2.28), whereas the 5–10 min extract was ranked the lowest (2.89). 10–15 min and 20–25 min extracts received intermediate appreciations (2.47 and 2.36 ranking, respectively). An LSD test revealed that 15–20 min and 20–25 min extracts were not significantly different (with 10% error), whereas they both significantly differed from the 5–10 min extract. We thus decided to use a 15–25 min extract for subsequent GC-O analyses.

It should be noted that the interpretation of overall hedonic results covers inter-individual differences in sensory preferences. In fact, six of the thirty eight panellists preferred the early extract of baking (5–10 min sample). The hedonic test was considered the best sensory test to apply to the present study because it could give a clearer understanding of the dynamic generation of aroma compounds involved in the pleasant odour of a baking cake. Moreover, preliminary results showed that, because of the highly pleasant character of such samples, sensory subjects had the tendency to rate baking odours according to their own preference even when they were asked to rate the intensity or similarity of cake-like odours.

In addition to these points, the analysis of the free semantic descriptors generated during the Direct-GC–Olfactometry (D-GC–O) session for each SPME fraction helps explain these hedonic results: the "5–10 min" SPME sample was, in fact, mainly characterised by an "unpleasant" note, whereas the extracts of the late baking intervals were associated with the "cake crust" and "baking cake" notes which were reported to be maximal for the "15–20 min" sample. This rapid technique (less than 3 min for the whole test) is suitable for sensory tests demanding a large number of assessors.

3.2.4. Determination of odour active compounds in baking vapours

As the SPME extracts obtained at the final stages of baking were the most interesting from the sensory point of view while not statistically different, we decided to submit the 15–25 min baking fraction to GCO and the frequency of detection method in order to identify the main key odorants responsible for odour quality. Results are reported in Table 1. More than 20 odour zones were detected but only odours associated with an identified compound and with a high frequency of detection are shown. A very intense and broad odour zone characterised by a "perfumed rice/cake/crust" descriptor was detected at 100% in the sample, it covers 2,5-, 2,6-, and 2,3-dimethylpyrazine, thus not allowing discrimination. Other very intense and consensual odours were found in correspondence with octanal ("citrus/floral"), hexanol (green/vegetal/cardboard), furfural ("cake/crust"), and acetylpyrazine ("hazelnut/praline/cake"). Moreover, amongst the high LRI compounds, furaneol, dodecanal, and 2,4-decadienal isomers were easily detected by sniffers. Pozo-Bayon et al. (2007) also found 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, octanal, 1-octen-3-ol, hexanol, furfural, phenylacetaldehyde, and (*E,E*)-2,4-decadienal as odour active compounds in a SAFE extract of crust and/or crumb of a sponge cake elaborated under the same conditions as in the present work. It should however be stressed that the present results were obtained using only four assessors. Actually, a larger panel could give richer information. Moreover, recombination experiments should be run in order to thoroughly identify the key impacting aroma compounds.

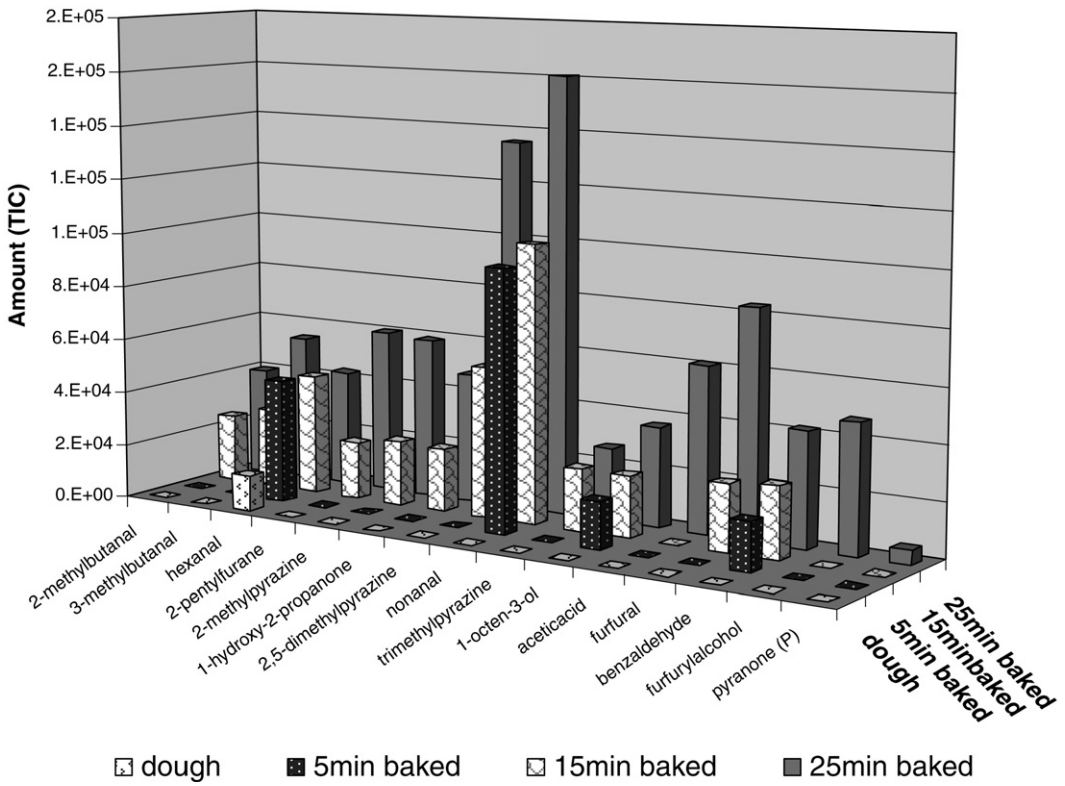

Fig. 4. Volatile compound composition of dough and sponge cakes baked for 5, 15 and 25 min. Samples were analysed by Static HS-SPME (DVB/Car/PDMS).

3.2.5. Determination of aroma compounds from baked cake matrix

In order to better understand the relationships between the dynamic release of volatile compounds during baking and their formation-increase in the matrix, the composition of sponge cake volatile compounds was also followed in samples baked for the three different durations (5, 15, and 25 min) under the same process conditions as previously described. Fig. 4 shows the evolution of the main volatile compounds versus baking time and relative to a dough sample. Maillard reaction related compounds were found in cake samples mainly after 5 min baking. On the other hand, lipid degradation related compounds such as hexanal, nonanal, and 1-octen-3-ol were detected very early in cakes (5 min of baking). In dough samples, only hexanal was found in detectable amounts under our experimental conditions. However, its amount in cake samples did not follow the same trend as in baking vapours (Fig. 2). Finally, HMF was not detected in the static HS-SPME extracts of sponge cake. This result is not surprising because of its low volatility ($B.P._{HMF}$: 110 °C at 0.02 mmHg, Merck index) and its low amount in the cake crust. Complementary quantitative HPLC analyses on the cake crusts following Ait Ameur et al. (2006) Ameur et al. (2006), showed indeed quantifiable amounts of HMF only in the 25 min baked samples (8.1 ± 0.1 mg/Kg dry matter). The amount of such compound seems to be strictly related to the processing parameters: in a recent work we found very high amounts of HMF (1100.1 ± 22.4 mg/Kg DM) in a model cookie submitted to strong thermal treatment (300 °C for 6 min) and having a moisture content twenty fold lower than the sponge cake crust (1.1% vs. 20.8%, respectively, Ait Ameur et al., 2008).

These results show that dynamic on-line HS-SPME on baking vapours could reliably follow the evolution of newly formed volatile compounds in a wide range of physicochemical properties. In further studies it would be interesting to compare static HS-SPME with other extraction methods (i.e. SAFE or solvent extraction) in order to avoid any eventual discrimination effect due to SPME extraction conditions. However all extraction methods have side-effects and suffer matrix effects, so sensory and chemical validations would be required. Moreover, a precise determination of volatile compound concentrations in the food matrix (i.e. by using stable isotope dilution) would be of great interest for further kinetic approaches.

4. Conclusion

This work shows that using a dynamic SPME device combined with an instrumented oven, it is possible to monitor the release of a large amount of volatile compounds generated during the baking of a model sponge cake by directly sampling its baking vapours. This on-line approach has the advantage of not perturbing the development of the food structure nor the thermal reactions occurring during the thermal process of baking. The steam assisted dynamic SPME device made it possible to extract volatile compounds with very different volatility and hydrophobicity, thus allowing very polar compounds like HMF and very volatile ones like 2-methylpropanal to be simultaneously detected. This advantage made it possible to simultaneously follow the release of several aroma compounds and thermal reaction markers at different stages of their generation in a sponge cake model by both sensory and chemical analyses. These results are encouraging for further developments aimed at understanding reaction kinetics in real food systems under strictly controlled process conditions.

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