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Keywords:
Solid food model, Maillard reaction, caramelization, Strecker degradation, reaction pathways, process parameters, temperature, thermal desorption, cereal product, leucine, glucose, aroma

Highlights:

- Specially designed hydrocolloid/starch-based model cake was non-reactive while baking
- Addition of specific precursors activated Maillard and/or caramelization reactions
- 20 markers semi-quantified by TD-GC-MS on vapors from precursor-containing cakes
- TD enables to quantify volatile markers after kinetic on-line dynamic extraction

Abstract:
This study presents a novel strategy for the dynamic analysis of volatile compounds extracted from baking vapors using a fit-for-purpose model cake. This model imitates a real sponge cake in terms of structure and processing but it is not reactive towards Maillard and caramelization reactions. When implemented with precursors (glucose (*G*) or glucose + leucine (*G+L*)), the reactions are activated and volatile markers can be monitored dynamically during baking. A method for the on-line sampling of vapors during baking using sorbent tubes coupled to thermal desorption (TD-GC-MS) has been developed and proven to be an appropriate and rapid technique to analyze a large number of volatile compounds within a broad range of physical and chemical characteristics. Volatile markers such as acetic acid, furfural, furfuryl alcohol and 5-hydroxymethylfurfual were identified using both models: glucose (*G*) and glucose+leucine (*G+L*) because they arise from both caramelization and the Maillard reaction. On the other hand, 3-methylbutanal and 2,5-

dimethylpyrazine were only identified in the (*G+L*) model cake as they arise from the Strecker degradation pathway induced by the presence of leucine. Moreover, the relative abundance of all markers of reactions covers a broad range. On-line sampling coupled to TD-GC-MS enabled the collection of kinetic data on these markers throughout the baking operation and discrimination of the two formulas (G *vs* G+L) and two baking temperatures (170°C and 200°C) used. These results offer promise for the further use of this approach to study reaction kinetics in model cakes.

1 Introduction

In all food products that contain reducing sugars and proteins and are subjected to thermal treatments (drying, pasteurizing, baking, roasting), the Maillard reaction and caramelization are responsible for the development of a brown color and specific roasted or sweet tastes or aromas (odors of chocolate, roasted nuts, roasted almonds or sweet burnt sugar (Cha, Debnath, & Lee, 2019). In particular, browning or the generation of aroma compounds during the baking of cereal products has been widely studied (Cerny, 2010; Golon, Javier, Da, & Kuhnert, 2013; Starowicz & Zieliński, 2019). In recent years, it has also been shown that these reactions may be responsible for the formation of undesirable toxic compounds, which include furanic compounds (Cepeda-Vázquez, Rega, Descharles, & Camel, 2018), acrylamide (Stadler et al., 2002), heterocyclic amines and advanced glycation end products (Teng, Hu, Tao, & Wang, 2018). Mastering the thermal reactivity of processed foods by fine tuning formulations and processes is therefore of crucial importance to food quality and safety.

The chemistry of the Maillard reaction, first described by Maillard in 1912 and formalized by Hodge in 1953, is a complicated cascade of numerous parallel and consecutive pathways leading to a large number of possible intermediate and final products. In a complex food, the Maillard reaction almost always interacts with other pathways such as caramelization and lipid oxidation (Hidalgo, Alaiz, & Zamora, 1999). This markedly hampers any comprehensive understanding of reactivity and its control in foods. Many studies have therefore been conducted in liquid and semi-liquid model systems focused on specific pathways thanks to the use of selected precursors (Gökmen, Kocadağlı, Göncüoğlu, & Mogol, 2012; Jusino, Ho, & Tong, 1997; Rainer Cremer & Eichner, 2000). The use of fully agitated liquid systems is an appropriate method to discriminate specific reaction pathways, but the results are little transferable to solid foods. Indeed, in a solid food subjected to thermal treatments, the mobility of precursors is reduced and structural and thermal heterogeneity needs to be taken into account because of their local impact on the reactions.

Kinetic reaction data and modelling are required to better understand the response pathways involved. Kinetic modelling can be of considerable assistance to better understanding the reaction pathways in food products, as it is a robust tool to clarify the rate-determining steps in complex reactions and thus understand their mechanisms (De Vleeschouwer, Van der Plancken, Van Loey, & Hendrickx, 2009; Martins, Jongen, & van Boekel, 2000). However, this approach requires accurate measurements of a considerable number of reaction

markers and suitable reaction media to study kinetics in a controlled environment in terms of the quantity and nature of reaction precursors. Aroma compounds, largely studied for their properties during baking (Takei, 1977; Ait Ameur et al., 2006, 2007; Dury-Brun et al., 2007; Rega et al., 2009; Paraskevopoulou et al., 2012; Pacyński et al., 2015; Cepeda-Vázquez et al., 2018), are also interesting in this manner since they can be considered as reaction markers. The amount of information on reaction pathways is proportional to the number of volatile compounds extractable and measurable.

The on-line dynamic sampling of volatile compounds from the oven is an interesting and non-destructive method to analyze large quantities of reaction markers simultaneously during baking. This method was recently used during baking studies on real cereal products by several authors (Fehaili, Courel, Rega, & Giampaoli, 2010; Maire, Rega, Cuvelier, Soto, & Giampaoli, 2013; Rega, Guerard, Delarue, Maire, & Giampaoli, 2009) and is mainly based on solid phase micro-extraction (SPME), a method that has been widely applied in the environmental and analytical chemistry fields. Although it is a sensitive and rapid extraction method adapted to online extraction during product processing, it nevertheless remains limited to qualitative or semi-quantitative applications and has the drawback of being fragile and poorly reproducible (high inter-fiber variability) when several fibers are used at the same time to perform dynamic sampling over a long period of processing.

Thermal desorption (TD) is a sampling technique that can extract and concentrate volatile molecules from vapor samples. TD has been used extensively to analyze air pollutants (Maret, 2013) or aroma compounds (Allwood et al., 2014; Gallego, Roca, Perales, Sánchez, & Esplugas, 2012). Cognat, Shepherd, Verrall & Stewart (2012) compared the SPME and TD techniques regarding the analysis of fresh and rancid oat cereal products. While producing similar results in terms of the volatile compound profile, both methods also demonstrated satisfactory performance regarding the presence of a suitable calibration step. The TD technique thus appears very promising for on-line sampling coupled to GC/MS analyses because of its robustness, its higher concentration capacity than SPME, its stability in terms of conservation and its high analytical throughput. To the best of our knowledge, this technique has never previously been applied to kinetic studies in a baking context.

A solid food model was very recently developed by Bousquières, Bonazzi and Michon (2017). This food model imitates sponge cake in terms of its structure and manufacturing method insofar as it develops an alveolar structure very similar to that of a true sponge cake using the same operations of mixing, foaming and baking. However, this solid food model does not contain any reactive ingredients as it has been formulated by replacing all of them (sugar, flour, eggs) with non-reactive ingredients (hydrocolloids, starch, water).

The aim of this study was to demonstrate the suitability of the model cake for studying the Maillard and caramelization reaction pathways in a comprehensive and discriminant manner by introducing *ad hoc* precursors (Leucine, Glucose) into the inert cake. Glucose was chosen because it is a simple reducing sugar

participating in both caramelization and the Maillard reaction. Leucine was chosen since it is one of the 8 essential amino acids and the precursor of 3-methylbutanal (3-MEB) (Zehentbauer & Grosch, 1998), key aroma compound of cereal products. The second goal was to develop TD on-line dynamic vapor extraction of volatile markers and demonstrate the feasibility of this technology for studying the reaction kinetics activated during the baking of precursor-containing model cakes.

2 Materials and Methods

2.1 Ingredients and reagents

The ingredients used for the real sponge cake were whole eggs (Ovipac, Ovoteam, Locminé, France), sucrose (Tereos, Lille, France) and wheat flour (Grands Moulins de Paris, France).

The ingredients used for the model cake were Ultrapure water (Milli-Q®), produced using an Integral 3 water purification system from Millipore®, native corn starch (Cargill, Minneapolis, USA) with a water content of 12.4% w/w (measured according to NF norm V05 707), and food grade cellulose derivatives (Dow Chemical, Midland, USA): methylcellulose (MC) type SGA7C and hydroxypropyl methyl cellulose (HPMC) type K250M). D-(+)-Glucose, used as a precursor, was supplied by Roquette Frères (Lestrem, France) and L-Leucine (Food Grade, ≥99%) came from Sigma-Aldrich (St. Louis, USA).

Furan (≥99%), hexanal (≥98%), 2-pentylfuran (≥98%), 2,5-dimethylpyrazine (2,5-DMP) (≥99%), 2,3,5-trimethylpyrazine (2,3,5-TMP) (≥99.9%), furfural (≥99%), benzaldehyde (≥99%), 5-hydroxymethylfurfural (HMF) (≥99%), 3-MEB (>99%) and ammonia solution at ~25% (LC-MS grade) were all purchased from Sigma-Aldrich (St. Louis, USA). Water, acetonitrile and methanol used for glucose and fructose analysis were purchased from Carlo Erba (Val-de-Reuil, France). D-(+)-Glucose (≥99.5%), D-(-)-Fructose (≥99%), acetic acid (≥96%), methanol (≥99.9%), Carrez Reagent I and II, 30% formaldehyde and 0.005 N NaOH solution were also supplied by Carlo Erba (Val-De-Reuil, France).

2.2 Batter preparation and baking conditions

For the real sponge cake (R), 237 g whole eggs and 131.5 g sucrose were mixed together for 10 min with a planetary mixer (Kitchen Aid model 5KSM150, Benton Harbor, USA) equipped with a vertical whisk at speed 10. A quantity of 131.5 g flour was gradually added at speed 2 for 40 s, and the mixture was then blended for 1 min 50 s at speed 2.

Model sponge cakes were prepared according to the method developed by Bousquières et al. (2017) using a hydrocolloid solution of HPMC and MC foamed with starch prior to baking. Glucose and leucine were added to the inert model cake (*I*) as specific precursors of reaction pathways. The amount of glucose was selected according to sugar content in a reference sponge cake, whereas leucine was chosen based on the content in

free amino acids and total free amino groups measured in the same reference product and considering that free amino acids are more reactive than proteins (Srivastava et al., 2018).

For each baking experiment, seven rectangular aluminum pans (8 × 4.3 × 3.5 cm) were each filled with 60 g batter and baked in an instrumented pilot oven with precise and uniform control of temperature (170°C or 200°C) and a high level of convection (Bongard, Wolfisheim, France) (Fehaili et al., 2010).

2.3 Cake sampling during baking and sample preparation for precursor analysis

In order to measure the evolution of precursor concentrations, model cakes were sampled from the oven at different times (6, 12, 24, 33, 56, 75, and 90 min) during a baking experiment at 200°C under high ventilation. They were then sealed immediately (Multivac, Lagny-sur-Marrie, France) in previously tared aluminum bags and plunged into a water/ethanol bath at -8°C for a minimum of 15 min in order to halt any further reactions. The samples were then stored at -20°C for 24 to 48 hours before being frozen at -80°C for 24 hours and freeze-dried at 0.003 mbar under a condenser temperature of -85°C (Martin Christ, Osterode am Harz, Germany). Finally, the freeze-dried samples were ground for 1 min using an electric chopper (Moulinex, Ecully, France), divided into eight aliquots and stored frozen at -20°C until they were used for analysis.

2.4 Glucose and fructose quantification using UHPLC-CAD

Monosaccharides were extracted at 20°C (0.4 g of freeze-dried sample/20 g Ultrapure water). After homogenization with a vortex for 30 s/3000 rpm, the extract was centrifuged at 5000g for 15 min, and then 10 g of supernatant were mixed with 0.5 mL Carrez I and 0.5 mL Carrez II reagents. The solution was homogenized with a vortex for 30 s/3000 rpm, then centrifuged at 10,000g for 2 min. The supernatant was filtered through a 0.2 µm hydrophilic nylon membrane (Fisher Scientific, Hampton, USA) and placed in a vial.

The glucose and fructose concentrations were quantified by UHPLC using a Thermo Fisher Dionex (Waltham, USA) U3000 system equipped with a trinary solvent manager RS pump, a refrigerated RS autosampler and a column oven RS Column compartment, coupled to a Corona™ Veo™ RS Charged Aerosol detector (CAD). The stationary phase was an Acquity BEH Amide column (Waters, Milford, USA), heated at 35°C with dimensions of 100 x 2.1 mm; 1.7 µm porous spherical particles. A Vanguard precolumn (5 x 2.1 mm) (Waters, Milford, USA) with the same stationary phase had been connected previously to the analytical column.

The mobile phase was composed of Water (A) and Acetonitrile (B), both alkalinized with 10 mM NH_4OH, flowing at 0.26 $mL.min^{-1}$. The gradient started at 20% A, was maintained for 4 min then reached 50% A in 3 min, this composition being kept for 3 min to rinse the system before returning back to 20% A in 0.5 min and finally equilibrating for 8.5 min, the total run duration being 19 min. The data were processed using Chromeleon® v7.2 software.

Calibration with an external standard method was used. The response range was evaluated for concentrations ranging from 0.01 to 3 $g.L^{-1}$ at 4-6 points. The response was quadratic with the concentration on the ordinates

and the peak area on the abscissa, without forcing the zero. The *LOD* and *LOQ* values for glucose were equal to 7.803 and 26.01 $mg.L^{-1}$, respectively, while for fructose they were equal to 9.339 and 31.13 $mg.L^{-1}$, respectively.

2.5 Quantification of free NH_2 by titration

Concentrations of free amino groups were measured by basic titration using the Sörensen method, where 0.038 g of a freeze-dried aliquot was suspended in 20 mL Ultrapure water and homogenized with a stirrer. Sample titration was fully automated using a Metrohm 809 Titrando titrator equipped with an autosampler (814 USB, Sample Processer, Metrohm, Herisau, Switzerland), and controlled by Tiamo v1.2.1 software. 15 mL of 30% formaldehyde were added to 20 mL of the solution brought to pH 8.5. The resulting acidity was titrated with a 0.005 N NaOH solution up to pH 8.5. The NaOH volume was used to calculate the concentration of free amino groups expressed in moles of NH_2 per gram of dry matter.

The linearity range of this method was evaluated for concentrations ranging from 0.0039 to 0.0382 $mmol.g^{-1}$ at six points. The *LOD* and *LOQ* values were equal to 0.761 and 2.536 $\mu mol.g^{-1}$, respectively.

2.6 Determination of dry matter content

The dry matter content of freeze-dried aliquots was determined by desiccation for 24 h at 105°C in a ventilated oven. The moisture content of the cakes was calculated from the difference in mass between the initial dough (precision 10^{-2} g) and the sampled cake (precision 10^{-4} g).

2.7 Determination of the level of browning using image analysis

Images of the upper surface of the model cakes were taken using a EOS 1300D digital camera (Canon, Japan) in manual mode (f = 4.0, speed 1/200, and ISO100). The cakes were placed on blue paper card in a uniformly illuminated environment, with an angle between the camera lens axis and the lighting source axis of 45º to prevent diffuse reflection. The images were taken on the day after baking and then treated (thresholding and conversion to shades of gray) using ImageJ®. The distribution of the number of pixels by L^* values was obtained (between 0 et 100, CIE*Lab* color scale). After determining the level of threshold making it possible to discriminate the color of model cakes ($L^*_{threshold}$ = 75), the level of browning was calculated according to Equation 1.

Equation 1. Calulation of the level of browning

$$Level\ of\ browning\ (\%) = \frac{Number\ of\ pixels\ for\ L^* < L^*_{threshold}}{Total\ number\ of\ pixels} \times 100$$

2.8 On-line extraction of baking vapors by sorbent tubes

Volatile compounds were extracted during baking using Air Toxics™ sorbent tubes (Perkin Elmer, Waltham, USA) connected to the internal atmosphere of the oven *via* a deactivated and silanized glass column (4.5 mm

of internal diameter, 18 cm of length), linked on the other side to a VCP 130 vacuum pump (VWR, Grafton, USA). A float flowmeter (Serv' Instrumentation, Lyon, France) enabled the extraction flow to be fixed at 50 mL/min during baking. Prior to any experiment, the oven was heated at 300°C for 1 hour under the same extraction flow in order to prevent any contamination, and the glass columns were rinsed with distilled water and dried after each baking experiment.

Baking vapors were sampled for 4 min at different time points during processing (0-4, 6-10, 24-28, 33-37, 58-62, and 88-92 min). This duration was long enough to collect sufficient quantities to meet the analytical limits, and short enough to discriminate the kinetic points during baking. A median time was then attributed to each kinetic point. After removing the sorbent tubes, they were sealed immediately with Teflon® caps, stored at ambient temperature and analyzed within the day.

2.9 Analysis of volatile compounds using TD-GC-MS

2.9.1 Thermal desorption of sorbent tubes

The desorption of Air Toxics™ tubes was performed with an automated TurboMatrix 650 thermal desorber (Perkin Elmer, USA). A dry air purge was applied for 10 min at 50 mL/min. Helium was used as the carrier gas. A first desorption was performed at 300°C for 10 min at 30 mL/min when the compounds were focused on a Tenax® cold trap at -20°C and then sent to the GC column by rapidly heating the trap from -20 to 280°C at 40°C/s, with an outlet split of 20 mL/min. In this manner, 16.7% of the gas volume of the volatile compounds desorbed from a sorbent tube was transferred to the GC system at a constant gas flow rate of 4 mL/min *via* a transfer line heated at 270°C. After each injection, the trap was cleaned by setting the hold time to 30 min at 280°C. The sorbent tubes were systematically conditioned after each analysis by heating at 330°C with a gas flow of 70 mL/min for 30 min.

2.9.2 GC-MS analysis of thermally desorbed volatile compounds

The volatile compounds were analyzed using a Trace 1300 Thermo Scientific gas chromatograph (Waltham, MA, USA) equipped with a DB-Wax GC column (60 m × 0.25 mm × 0.5 µm) coupled with an ISQ QD (Thermo Scientific, USA) mass spectrometer. The GC oven temperature was held at 80°C for 5 min, then raised to 170°C by increments of 4°C/min and then 240°C at 10°C/min, and was finally maintained at 240°C for 20 min. The MS transfer line and ion source temperatures were set at 270°C and 200°C, respectively. The ionization mode was electron impact (EI), at 70 eV. Mass detection was carried out in full scan and a selected ion monitoring mode over a mass range of 25-250 amu at 0.4 s per scan. The compounds were identified by comparison with the Wiley 8 and NIST 08 mass spectra databases, calculation of the normal alkane retention index (*RI exp*) and a comparison with the retention index from the NIST Chemistry WebBook (*RI ref*) and an analysis of pure standards. Chromatographic peak areas and heights for each compound were calculated using Xcalibur 2.1.0 SP1, build 1160 (Thermo Fisher Scientific Inc., USA).

LOD and *LOQ* were estimated from an analysis of blanks, with a signal-to-noise ratio of 3 and 10, respectively.

2.9.3 Reproducibility, recovery and repeatability of extraction by sorbent tubes

Reproducibility, recovery and repeatability were assessed using a standard solution of nine compounds with different volatilities, typical of a sponge cake (Rega et al., 2009; Cepeda et al., 2017; Fehaili et al.; 2010), diluted at 0.1 $g.L^{-1}$ in methanol, a solvent that is not retained by Air Toxics™ tubes. 1 µL of this solution was vaporized at 250°C in the GC injector, then carried through a 1 m long deactivated silica capillary for 3 min (with helium as the carrier gas; 50 mL/min) to the sorbent tubes, which were then thermally desorbed and analyzed by GC-MS as previously described.

3 Results and Discussion

3.1 Analytical performance of the thermal desorption method for selected volatile compounds

The analytical performance of sorption on Air Toxics™ tubes, and desorption and analysis by TD-GC-MS, was tested on a broad range of compounds with different volatilities and polarities (Table1). Reproducibility was assessed from the variation coefficients of the chromatographic peak areas for each compound over 12 different sorbent tubes, and from successive thermal desorption procedures performed twice on the same sorbent tube. Recovery was calculated as the ratio of the peak area obtained for the first desorption ($Area_{D1}$) to the sum of the peak areas obtained for both desorptions ($Area_{D1} + Area_{D2}$). Repeatability was determined by calculating the variation coefficient of the chromatographic peak areas of each compound over five repetitions on the same sorbent tube.

Table 1. Analytical performance of sorbent tubes for selected volatile compounds

			Chemical characteristics				Analytical performance		
Compound	CAS No	Reaction pathway[a]	Formula	log K_{ow}[b]	Pv at 25°C (mm Hg)[b]	K_H ($atm.m^3.mol^{-1}$)[b]	Reproducibility (%)	Recovery (%)	Repeatability (%)
Furan	110-00-9	MR, C, LO	C_4H_4O	1.34	600	5.4×10^{-3}	8.5	100	18.6
Hexanal	66-25-1	LO	$C_6H_{12}O$	1.78	11.3	2.13×10^{-4}	24.4	100	9.1
2-pentylfuran	3777-69-3	MR, LO	$C_9H_{14}O$	3.87	1.2	1.84×10^{-2}	10.1	99.7	5.9
2,5-dimethyl pyrazine	123-32-0	SD	$C_6H_8N_2$	0.63	3.18	3.55×10^{-6}	8.6	100	9.8
2,3,5-trimethyl pyrazine	14667-55-1	SD	$C_7H_{10}N$	0.95	1.45	3.92×10^{-6}	9.7	100	11.3
Acetic acid	64-19-7	MR, C	$C_2H_4O_2$	-0.17	15.7	1.43×10^{-7}	*nd*	94.3	*nd*
Furfural	98-01-1	MR, C	$C_5H_4O_2$	0.41	2.21	3.8×10^{-6}	8.1	100	9.2
Benzal--dehyde	100-52-7	SD	C_7H_6O	1.48	0.127	2.67×10^{-5}	8.3	100	12.0
5-hydroxy methyl furfural	67-47-0	MR, C	$C_6H_6O_3$	-0.09	5.28×10^{-3}	5.41×10^{-10}	39.7	*nd*	27.3

[a]: from Maire et al. (Maire et al., 2013), MR = Maillard reaction, SD = Strecker degradation, C = caramelization, LO = lipid oxidation

[b]: from the Pubchem or EPI Suite™ v4.0 databases. Log K_{ow} is a measure of hydrophobicity. P_V and K_H indicate the volatility of the compounds.

nd = not determined

The results showed that the TD-GC-MS method selected enabled the extraction of 100% of most of the volatile compounds adsorbed in Air Toxics™ tubes, with excellent reproducibility (≤10%) and repeatability (≤20%). These values were less satisfactory for HMF, probably because of its weaker volatility which meant that the injection method chosen was less efficient.

3.2 Non reactivity of the model cake

The absence of possible Maillard or caramelization precursors in model cake *I* (inert, without any precursors) was first tested by measuring the concentrations of glucose, fructose and free amino groups in the batter and in model cakes baked under harsh conditions, *i.e.* at 200°C for different periods up to 90 min. All measured values were below the LOD. Starch could possibly be hydrolysed to D-glucose *via* an enzymatic or acid pathway (Kunamneni & Singh, 2005; Stevnebø, Sahlström, & Svihus, 2006), and Kunlan et al. (2001) also showed that heating would generally accelerate acid hydrolysis. Our measurements indicated that this hydrolysis was highly unlikely to happen in the present starch-based model cakes baked within a temperature range of 140°C to 200°C. Color determinations of inert model cake (*I)* also showed no signs of browning. These results therefore proved that any color changes to the model cake during baking would be solely due to reactions induced by supplementation with the precursors (reducing sugars and amino acids) leading to the formation of brown polymers. **Erreur ! Source du renvoi introuvable.** shows the presence of 23 typical reaction markers of the Maillard or caramelization reactions determined by TD-GC-MS in baking vapors from a real sponge cake (*R*). This result was in agreement with the existing literature and in particular with the results obtained using SPME on similar formulations (Maire et al., 2013; Rega et al., 2009). However, when the inert model cake (*I)* was analyzed under the same conditions, Table 2 shows that apart from acetic acid (for which the peak area was between LOD and LOQ), none of these volatile reaction markers could be detected, even under the most stringent baking conditions (up to 60 min of baking at 200°C). This finding was in line with that of a previous study by Srivastava et al., 2018, performed on a similar model cake, where no traces of furfural were detected (< LOD: 10.2 ng fufural/g sample dry basis).

In view of all these measurements, model cake (*I)* could be considered as a non-reactive product in terms of the Maillard and caramelization reactions and therefore suitable to study reaction pathways when supplemented with one or more precursors.

Table 2. Peak areas of volatile compounds measured from vapor using TD-GC-MS during baking at 200°C under high ventilation for a real sponge cake (*R*) and model cakes without (*I*) or with added precursors (*G* and *G+L*)

Class	Compound	CAS No	RI ref.[b]	RI exp[a]	Identifi-cation method[c]	Chromatographic peak area (a.u.*min)						
						R 30-34 min (n=1)	*I* 25-30 min (n=1)	*I* 55-60 min (n=1)	*G* 33-37 min (n=3)		*G+L* 33-37 min (n=2)	
									Mean	STD	Mean	STD
Aldehydes	2-methylpropanal	78-84-2	855	851	MS, RI	1E+08	<LOD	<LOD	<LOD		>LOD <LOQ	
	Butanal	123-72-8	904	916	MS, RI	>LOD <LOQ	<LOD	<LOD	<LOD		<LOD	
	3-methylbutanal	590-86-3	943	978	MS, RI, STD	6E+07	<LOD	<LOD	<LOD		9E+09	1E+09
	Pentanal	110-62-3	1003	1019	MS, RI	3E+07	<LOD	<LOD	<LOD		<LOD	
	Hexanal	66-25-1	1120	1119	MS, RI	3E+07	<LOD	<LOD	<LOQ		<LOD	
Ketons	2-butanone	78-93-3	926	939	MS, RI	3E+07	<LOD	<LOD	<LOD		<LOD	
	2,3-butanedione	431-03-8	1020	1010	MS, RI	8E+07	<LOD	<LOD	<LOQ		<LOD	
	2-pentanone	107-87-9	1005	1011	MS, RI	<LOD	<LOD	<LOD	<LOD		3E+08	2E+08
	2,3-pentanedione	600-14-6	1082	1093	MS, RI	<LOQ	<LOD	<LOD	<LOD		3E+07	2E+07
	1-hydroxy-2-propanone	116-09-6	1321	1361	MS, RI	1E+07	<LOD	<LOD	<LOD		<LOD	
	1-acetoxy-2-propanone	592-20-1	1484	1504	MS, RI	<LOD	<LOD	<LOD	<LOD		4E+07	2E+07
	2-cyclopentene-1,4-dione	930-60-9	*nf*	1654	MS	2E+08	<LOD	<LOD	<LOQ		6E+08	3E+08
Acides	Acetic acid	64-19-7	1488	1487	MS, RI, STD	6E+09	>LOD <LOQ	>LOD <LOQ	4E+08	6E+07	4E+09	1E+09
	Propanoic acid	79-09-4	1574	1578	MS, RI	<LOD	<LOD	<LOD	<LOD		5E+07	1E+07
	2-methyl propanoic acid	79-31-2	1588	1605	MS, RI	<LOD	<LOD	<LOD	<LOD		4E+08	2E+08
Pyrazine compounds	Pyrazine	290-37-9	1257	1260	MS, RI, STD	<LOD	<LOD	<LOD	<LOD		3E+07	1E+07
	Methylpyrazine	109-08-0	1283	1315	MS, RI, STD	4E+07	<LOD	<LOD	<LOD		2E+08	1E+08
	2,5-dimethylpyrazine	123-32-0	1348	1372	MS, RI, STD	<LOQ	<LOD	<LOD	<LOD		4E+07	2E+07
Furanic compounds	Furan	110-00-9	*nf*	822	MS	4E+08	<LOD	<LOD	<LOD		5E+08	6E+08
	3-methylfurane	930-27-8	*nf*	906	MS	5E+07	<LOD	<LOD	<LOD		1E+08	7E+07
	Furfuryl alcohol	98-00-0	1613	*nd*	MS, STD	1E+09	<LOD	<LOD	<LOQ		3E+08	1E+08
	Furfural	98-01-1	1493	1520	MS, RI, STD	4E+09	<LOD	<LOD	3E+09	4E+08	7E+09	2E+09
	5-methylfurfural	620-02-0	1604	1642	MS, RI, STD	1E+08	<LOD	<LOD	<LOQ		3E+09	2E+09
	5-hydroxy methylfurfural	67-47-0	2526	*nd*	MS, STD	6E+08	<LOD	<LOD	4E+08	2E+07	7E+08	4E+08

[a]: Retention index from the NIST (http://webbook.nist.gov/chemistry/) for a DB-Wax column and GC method comparable to the method used here.

[b]: Linear retention index (LRI) obtained using the Van den Dool and Kratz equation for non-isothermal GC program, on a DB-Wax column.

[c]: Compound identification: MS: mass spectroscopy library match (WileyRegistry8e data base); LRI: good correspondence with Van den Dool and Kratz Linear Retention Index from NIST; STD: compared with the injection of pure standard.

nd = not determined, *nf* = not found

3.3 Activation of reactions in model cakes supplemented with *G* and *G+L* at high temperatures

To promote and study caramelization specifically, or combined with the Maillard reaction, two models were designed by adding glucose (*G* model) or glucose plus leucine (*G+L* model) to the inert model cake *I*. Glucose was chosen as a reducing sugar and one of the principal monosaccharides traditionally used as a baking ingredient. Leucine is one of the eight essential amino acids and the specific precursor of 3-MEB, which is known to be responsible for fruity and cocoa notes in baked or roasted products (Salem, Rooney, & Johnson, 1967).

With model cake *G*, acetic acid, furfural and HMF were detected in relatively large quantities in the baking vapors collected after 33-37 min of baking at 200°C under high convection, thus proving that the caramelization of glucose had taken place. Under the same baking conditions, other volatile compounds such as 2-pentanone, 2,3-pentanedione1-acetoxy-2-propanone, 2-cyclopentene-1,4-dione, propanoic acid, 2-methylpropanoic acid, furan, 3-methylfurane, furfuryl alcohol, and 5-methylfurfural were also detected and quantified for model cakes *G+L*. Hexanal was detected suggesting that lipid oxidation may have taken place due to the lipids traces in the starch in a very small extent. Quite large quantities of 3-MEB were also detected, together with lower levels of pyrazine, methylpyrazine and 2,5-DMP, all of them indicating that Strecker degradation had taken place. All these compounds were found in a real sponge cake where 16 volatile compounds were quantified and three others detected after 30 min of baking under harsh thermal conditions (200°C, high ventilation) (**Erreur ! Source du renvoi introuvable.**). These results therefore indicated that the extraction and analytical methods used in this study were suitable for tracking the levels of a broad range of volatile markers typical of caramelization, Maillard reactions and lipid oxidation pathways that formed during baking.

3.4 Reactivity determined by the degree of browning in model cakes *G* and *G+L*

The images in Figure 1 clearly show the degrees of browning of model cakes containing precursors, as a function of both the composition in precursors and the duration and temperature of baking. Coloration occurred gradually in model cakes *G* and browning was quite slight, even after 90 min of baking at 200°C. Thus the caramelization reaction pathways induced relatively low levels of browning, with high activation energy. However, browning occurred quite rapidly and was more intense in the presence of leucine. This was a clear indication that the browning caused by the Maillard reaction is accelerated by the presence of an amino group and involves reaction pathways different from those observed without leucine. Moreover, it is worth noting that in both model cakes *G* and *G+L*, the cores of the cakes remained relatively white, while browning was mostly located in the dry crust at the surface (Srivastava et al., 2018). These results suggest the importance of the link between temperature and moisture gradients and the progress of reactions. It would therefore be interesting to be able to predict these gradients accurately in order to correctly describe reactivity in a solid product such as a cake.

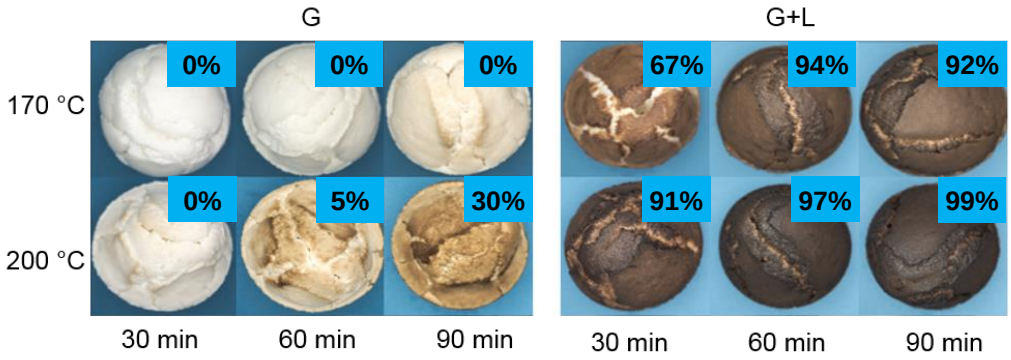

Figure 1. Photographs of model cakes sampled during baking at 170°C and 200°C

3.5 Kinetic study during baking at high temperature

Six compounds were selected for further kinetic studies: acetic acid, HMF, furfural, furfuryl alcohol, 3-MEB and 2,5-DMP. This choice was motivated by the presence of these compounds in the real sponge cake and similar products (Adams, 2005; Fehaili et al., 2010; Pacyński, Wojtasiak, & Mildner-Szkudlarz, 2015; Rega et al., 2009). This choice was based on their potential to enable the discrimination of different reaction pathways (Figure 2), their abundance from the start to the end of baking and the availability of standard solutions.

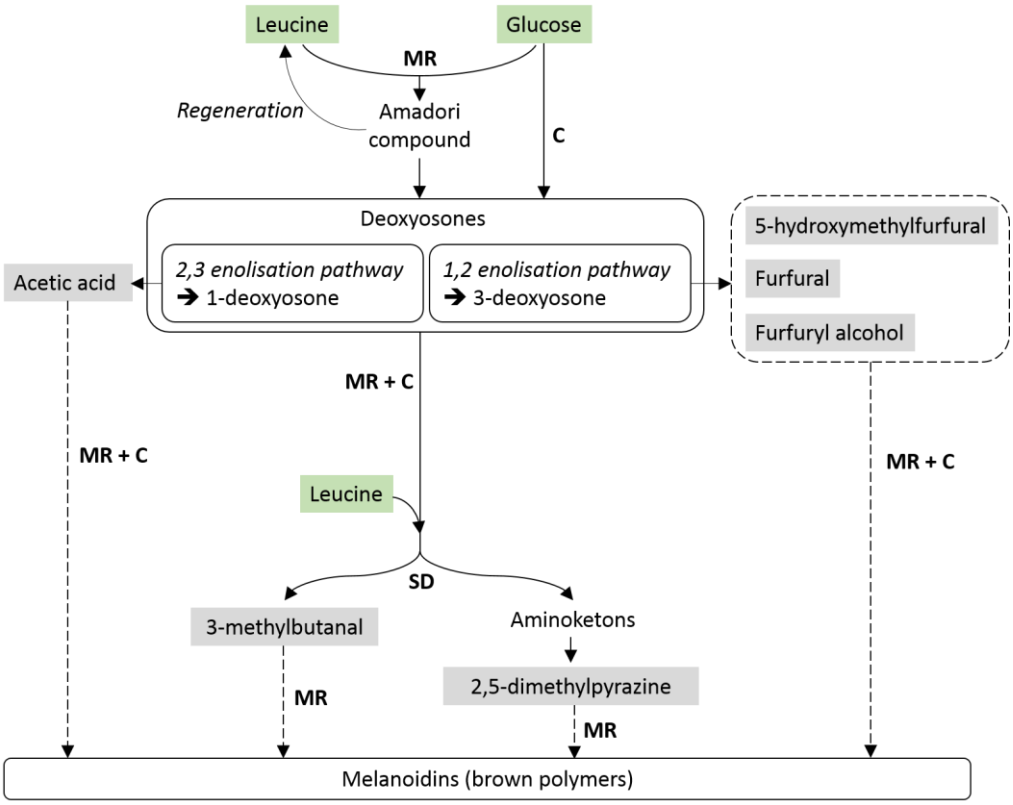

Figure 2. Simplified reaction diagram involving selected volatile markers. MR = Maillard reaction, C = Caramelization, SD = Strecker degradation

HMF is generated during the intermediate stage of the Maillard reaction and has therefore been used as a marker to monitor its progress (Rufián-Henares, García-Villanova, & Guerra-Hernández, 2008). HMF is also known to have a potentially toxic impact on human health (Pastoriza de la Cueva et al., 2017). Furfural is a compound with a characteristic bread-like and almond odor. Furfural is known to be generated *via* 1,2-enolization, both through the Maillard reaction and caramelization, *via* pentoses (Belitz, Grosch, & Schieberle, 2009; Kroh, 1994; Martins et al., 2000; Poinot et al., 2008) but its formation from glucose has also been reported (Srivastava et al., 2018; Yaylayan & Keyhani, 2000). Furfuryl alcohol is another a volatile compound that is generally generated during the baking of cereal-based products and has a burnt, warm oil note (Pico, Bernal, & Gómez, 2015). The formation of furfuryl alcohol *via* 3-deoxyosone has been postulated in the literature (Hollnagel & Kroh, 2002). Acetic acid can form *via* 1-deoxyosone and this pathway has been widely studied (Knol, Linssen, & van Boekel, 2010; Martins & van Boekel, 2005). 3-MEB is responsible for a dark chocolate and malty aroma. It is the Strecker aldehyde that arises from leucine, so was specific to the *G+L* model cake. 2,5-DMP is a volatile compound often found in bakery products that has a popcorn and potato-like note (Starowicz & Zieliński, 2019), and aminoketones that form during Strecker degradation can cause its formation (Jusino et al., 1997). On-line extraction and TD-GC-MS analysis made it possible to follow all these reaction markers during the baking experiments.

For model cakes *G*, the area of the chromatographic peak for furfural reported in **Erreur ! Source du renvoi introuvable.** was approximatively 10-fold larger than those of HMF and acetic acid (both being of the same order of magnitude), which were in turn 10-fold larger than the area of furfuryl alcohol. These relative proportions were very different for *G+L* cakes when both caramelization and Maillard reaction pathways were activated, indicating markedly different concentrations in the cakes. The kinetics determined for these four compounds and both formulas during baking at 200°C are shown in Figure 3. For the model cakes that only contained glucose, these compounds formed gradually during baking, and much higher levels of furfural were detected. When leucine was also added, all the kinetics accelerated. Furfuryl alcohol and acetic acid were detected at much higher levels. The curve for furfural revealed a plateau after 25 minutes of baking where the responses measured were in the same order of magnitude as for the *G* formula, while the curve for HMF was bell-shaped, indicative of its formation and rapid consumption. Given the linearity of the HMF response, these results showed that this compound degrades more rapidly in the presence of an amino group, most probably because it reacts to form melanoidins (Hodge, 1953; Martins & van Boekel, 2003). 2,5-DMP and 3-MEB could not be detected during the baking of the model cakes *G* under these relatively harsh conditions, whereas they were observed during the baking of *G+L*, confirming that the presence of a free amino group is necessary for their formation *via* Strecker degradation.

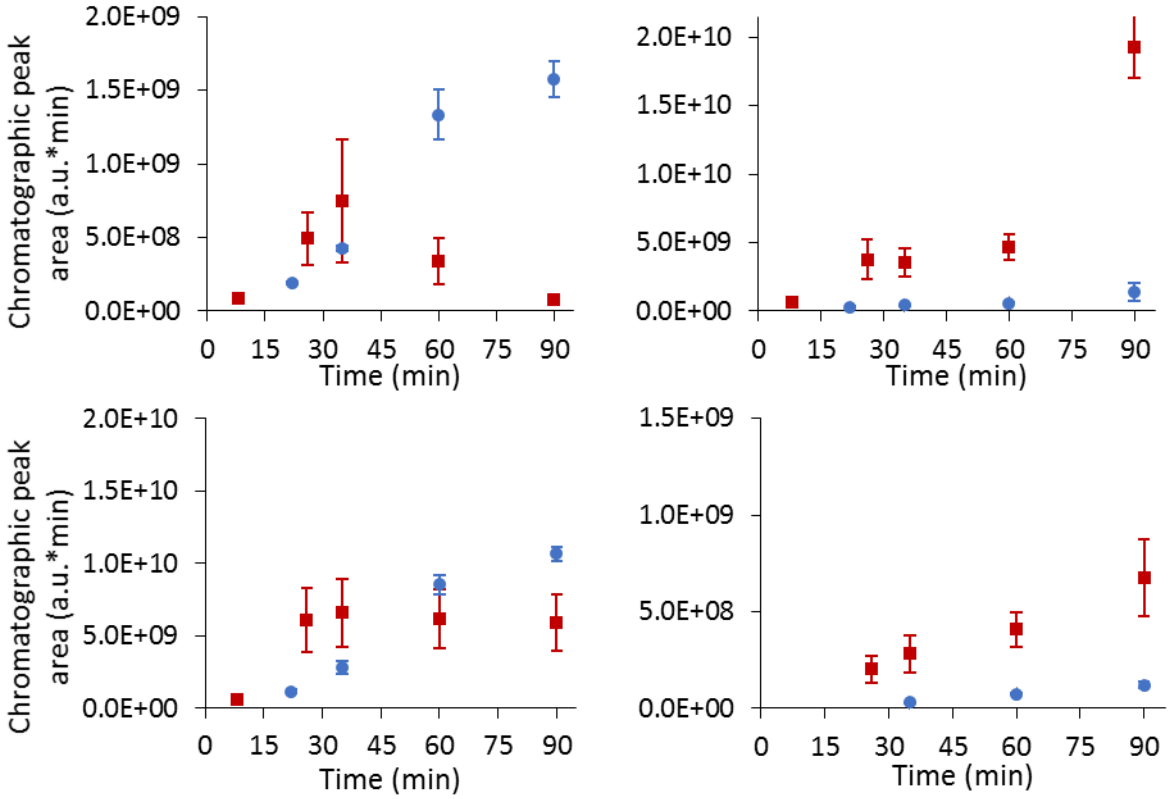

Figure 3 Chromatographic peak areas of HMF, acetic acid, furfural and furfuryl alcohol extracted from baking vapor and analyzed using TD-GC-MS at different time points during baking at 200°C under high convection of model cake *G* (●, n=3) or *G*+*L* (■, n=2)

3.6 Effect of baking temperature on kinetics

If we consider the formation kinetics of the same four volatile compounds through caramelization at 170°C or 200°C in *G* cakes (Figure 4**Erreur ! Source du renvoi introuvable.**), the higher the baking temperature, the higher the levels of compounds detected, particularly those formed *via* the 1,2-enolization pathway. It appeared clearly that the formation kinetics of all compounds were notably accelerated by temperature. In terms of the Strecker degradation markers in *G*+*L*, the results in Figure 5 show that an increase in temperature had no significant impact on the amount of 3-MEB formed, but appeared to accelerate the formation of 2,5-DMP. The slight decrease in the area of the chromatographic peak for 3-MEB under both temperatures after 30 min of baking indicated its potential consumption by another reaction. Tressl, Wondrak, Garbe, Krüger, & Rewicki, 1998 suggested the possible formation of melanoidins from 3-MEB. Our findings suggest that an increase in temperature might favor the 1,2-enolization pathway over the 2,3-enolization pathway. This is consistent with the fact that the increases in the relative quantities of HMF and furfural from 170°C and 200°C were greater than that of acetic acid. However, this hypothesis needs to be verified by specifically quantifying not only 1-deoxyosone and 3-deoxyosone, but also dicarbonyl intermediate compounds such as glyoxal and methylgloxal, as they can form 3-MEB and melanoidins (Guerra & Yaylayan, 2013; Pripis-nicolau, Revel, Bertrand, & Maujean, 2000).

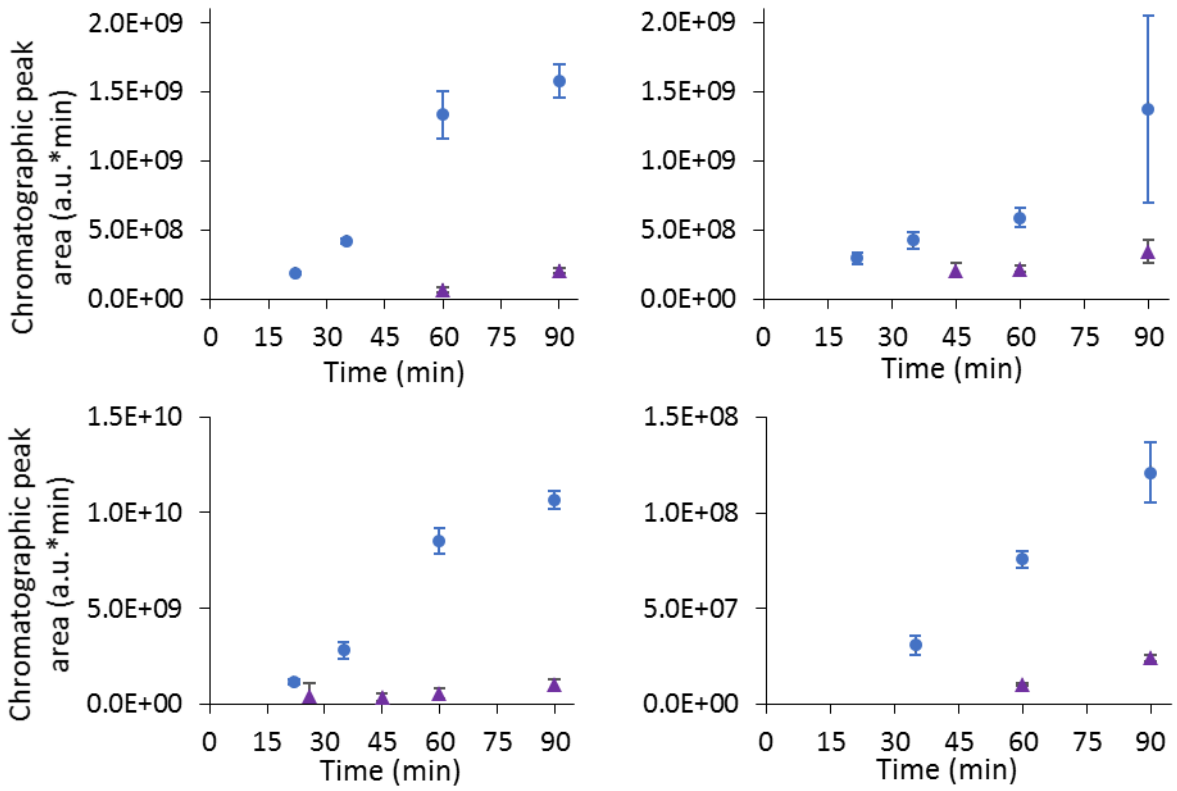

Figure 4. Chromatographic peak areas of HMF, acetic acid, furfural and furfuryl alcohol extracted from baking vapor and analyzed using TD-GC-MS at different time points during the baking of model cake (G) (●, n=3) at 200°C under high convection, and model cake (G) (▲, n=2) at 170°C under high convection

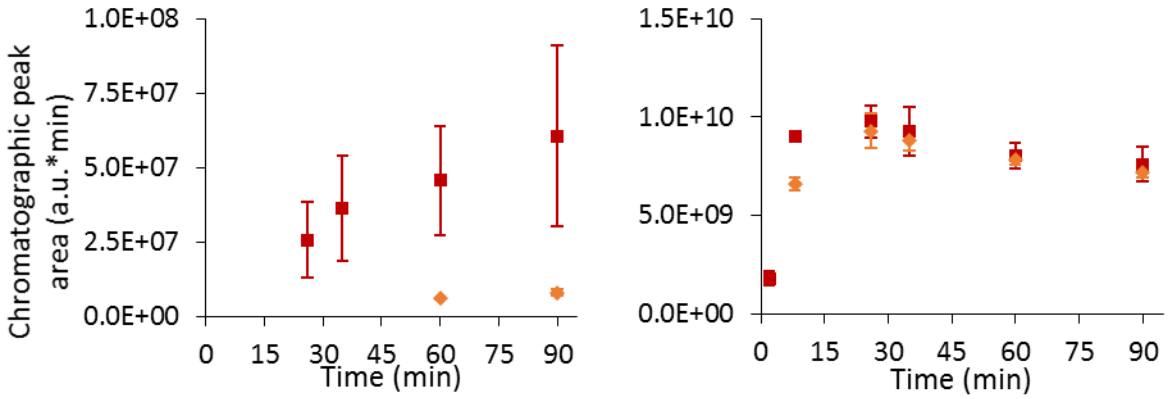

Figure 5. Chromatographic peak areas of 2,5-DMP and 3-MEB extracted from baking vapor and analyzed using TD-GC-MS at different time points during the baking of model cake (G+L) (■, n=2) at 200°C under high convection and model cake (G+L) (◆, n=3) at 170°C under high convection

4 Conclusions

It could be concluded that the model cake developed by Bousquières et al., 2017, and composed of starch, hydrocolloids and water, was non-reactive. When implemented with either glucose or glucose and leucine, the *G* and *G+L* cakes generated numerous volatile compounds typical of caramelization and/or Maillard reactions. Both formulations made it possible to highlight different reaction pathways, or at least activate them in different ways. The cake model has the advantage of leaving the possibility of adding precursors of choice.

For example, fructose or sucrose can be implemented in the cake model in which case the hydrolysis of sucrose to fructose and glucose can also be studied.

During the present study, 20 markers of bakery products could be identified and semi-quantified using on-line extraction and TD-GC-MS analysis (peak area response). Thermal desorption was indeed an appropriate and rapid qualitative technique for extraction throughout the baking and analysis of a large number of volatile compounds with different properties (e.g. volatility and hydrophobicity). Moreover, this approach was found to be effective indiscriminating between the two reactive systems (cakes *G* and *G+L*) and between two baking temperatures (170°C and 200°C). The sensitivity of all the reaction markers studied was sufficiently high to detect significant differences in the chromatographic responses obtained over very short and numerous sampling intervals that covered the entire baking duration of the model cakes. These results offer considerable promise for the further use of this approach to study reaction kinetics in model cakes through the quantitative determination of volatile markers as well as precursors and intermediates, in order to provide data for kinetic modelling and subsequent reaction engineering strategies.

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Conflicts of interest: none

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