

## Quantitative determination of volatile compounds using TD GC MS and isotope standard addition for application to the heat treatment of food.

J. Lee, S. Roux, N. Descharles, C. Bonazzi, Barbara Rega

### ► To cite this version:

J. Lee, S. Roux, N. Descharles, C. Bonazzi, Barbara Rega. Quantitative determination of volatile compounds using TD GC MS and isotope standard addition for application to the heat treatment of food.. Food Control, 2021, 121, 10.1016/j.foodcont.2020.107635 . hal-03925898

## HAL Id: hal-03925898 https://hal.science/hal-03925898

Submitted on 5 Jan 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Quantitative determination of volatile compounds using TD-GC-MS and isotope standard addition for application to the heat treatment of food.

#### Authors:

Lee, J., Roux, S., Descharles, N., Bonazzi, C., Rega, B.\*

Université Paris-Saclay, INRAE, AgroParisTech, UMR SayFood, 91300, Massy, France

\* Corresponding author: Barbara Rega, Paris-Saclay Food and Bioproduct Engineering Research Unit (SayFood), 1 Avenue des Olympiades, 91744 Massy Cedex, France. Tel.: +33 169935133; e-mail address: barbara.rega@agroparistech.fr

Other authors' e-mail addresses: jeehyun.lee@agroparistech.fr; stephanie.roux@agroparistech.fr; nicolas.descharles@agroparistech.fr; catherine.bonazzi@agroparistech.fr

#### **Keywords:**

Thermal desorption, on-line sampling, aroma, process-induced reactivity, newly formed compounds, Maillard reaction

#### **Highlights:**

- A novel quantitative method to determine volatile compounds in gaseous samples
- The assay combines volatile trapping, isotope standard addition and GC-MS analysis
- Markers with different chemical properties were quantified from ng to mg levels
- The method was applied to sample and measure newly formed compounds during baking
- This method is transferable to monitoring kinetics, other processes and VOCs

#### Abstract:

For many foods that undergo thermal treatment, the generation of numerous process-induced compounds has strong implications for food quality and safety. Today, increasing attention is payed to the generation and occurrence of particular classes of newly formed compounds in processed foods for their potential health implication. It is therefore of the utmost importance to monitor the process with fit-for-purpose methods that are appropriate for use in quality control or in research and innovation. Since many quality-related compounds are volatile, there is a need for robust methods that can quantify a broad range of volatile markers and are applicable to on-line monitoring.

To meet this need, an original and reliable method based on thermal desorption has been developed for the quantitation of volatile compounds sampled on-line by sorbent tubes. For the first time, this method combines in-tube calibration and deuterated standard addition. Ten volatile compounds that are likely to form during heat processing of food (i.e. baking of cereal products), were chosen as target analytes for their relevance to food quality and their different physicochemical properties: 3-methylbutanal, pyrazine, 2-methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, acetic acid, furfural, 5-methylfurfural,

furfuryl alcohol and 5-hydroxymethylfurfural. The key steps in the analytical procedure were optimized and carefully characterized in terms of recovery, repeatability and reliability. The TD-GC-MS method displayed good linearity over extended ranges for all compounds ( $R^2$ : 0.9950 to 0.8880) with low limits of quantification (*LOQ*s) ranging from 0.0141 to 11.5 ng. The matrix effect was negligible for most compounds, except for 5-hydroxymethylfurfural (21.5%), the most polar and least volatile compound.

The method was applied to determining process-induced compounds generated during the baking of a model cake and sampled from baking vapors at three different times during the heat treatment. Of all the compounds extracted, the target analytes exhibited concentrations spread over very broad ranges. This highly sensitive method could therefore be used for the early quantification of relevant markers during the processing of food matrices, for quality or mitigation purposes.

Quantitative TD-GC-MS with in-tube calibration and isotope standard addition is particularly well-suited for applications where an accurate determination is required of both trace level and major volatile compounds over time. This method may therefore be relevant for monitoring either industrial or domestic food processes (e.g. baking, frying, roasting), for multi-residue analyses linked to quality and safety, or reaction kinetics for multi-response modeling. It can also be transferable to emerging non-food applications.

#### **1** Introduction

The thermal treatment of food can trigger the formation of a large number of volatile compounds that affect quality. Indeed, food products contain reactants (sugars, amino acids and lipids) which may participate in the heat-sensitive reactions caused by heat treatments (drying, pasteurizing, baking or roasting). The impact of physical and chemical variables on the profile of volatile compounds has been studied extensively during recent decades, particularly in cereal and bakery products (Birch et al., 2014; Cho & Peterson, 2010; Hansen & Schieberle, 2005; M.A. Pozo-Bayón et al., 2006; Rega et al., 2009; Salim-ur-Rehman et al., 2006) from the angles of both flavor and food safety-related issues (Cepeda-Vázquez et al., 2018; Ozolina et al., 2011). The volatile compounds in bakery products mostly result from the Maillard reaction, caramelization and lipid oxidation (Grosch & Schieberle, 1997; Maire et al., 2013), with ingredients and process conditions being the main factors that affect their generation (Ait Ameur et al., 2008; Birch et al., 2014; Cepeda-Vázquez et al., 2019; Cho & Peterson, 2010; Maria Angeles Pozo-Bayón et al., 2007; Zhou et al., 1999). However, from a more comprehensive standpoint, thermally induced volatile compounds have been studied as markers of the degree of processing and more recently as markers of reaction kinetics (Srivastava et al., 2018). Whatever the purpose of the research (e.g. controlling final concentrations or understanding the phenomena that underpin the generation of process-induced markers) the analytical strategies to determine volatile compounds from foods remain a challenge because of their low concentrations, their different physicochemical properties and the variability of matrices and processes (Elmore, 2015; Xu et al., 2016; Zhou et al., 1999).

The most widely applied solvent-free extraction methods for volatile compounds include headspace (HS) techniques such as SPME in headspace sampling mode (Elmore, 2015; Sgorbini et al., 2019). Static Headspace is a rapid and simple sampling method (Paik & Venables, 1991) and provides a very good odor representation of extracts (Rega et al., 2003), but, it often lacks sensitivity compared to dynamic HS and HS-SPME (Crews & Castle, 2007). HS-SPME has been widely used for the screening and qualitative analysis of a large number of volatile compounds from solid and liquid products and it is also used extensively for foodomics applications due to its high throughput characteristics (Moreira et al., 2019; Pico, Antolín, et al., 2018; Pico, Tapia, et al., 2018). However, this method is poorly applicable to the assay of a large number of volatile compounds during processing, because their partition coefficients between the headspace and the fiber differ and are impacted by many factors such as polarity, volatility and molecular weight of the compounds (Zhang et al., 2018).

In the case of specific applications such as kinetic studies and kinetic modeling, the HS and HS-SPME methods have limitations when quantitative measurements are required (Fehaili et al., 2010; Parker, 2013; van Boekel, 2001). Recently, HS trap extraction coupled to isotopic dilution was developed for the quantification of two reaction markers (furan and furfural) from sponge cakes (Cepeda-Vázquez et al., 2016; Srivastava et al., 2018). Despite the fact that this technique is highly sensitive (ppb levels) and robust, it is not applicable to a large number of volatile markers and to determining numerous experimental points for kinetics studies since it is destructive and time-consuming.

Many studies have indicated the potential of the on-line sampling of baking vapors in order to identify and follow for kinetic purposes a large number of volatile markers throughout thermal processing (Fehaili et al., 2010; Poinot et al., 2010; Zanin et al., 2020). However the quantification of volatile compounds has remained a bottleneck with these methods.

There is therefore a need for high throughput methods that can both sample on-line and quantitatively analyze volatile compounds during thermal processing for the purposes of monitoring and modeling kinetics. Thermal desorption (TD) could be a good candidate as shown by the rising interest and increasing number of scientific papers on its applications. Despite the fact that TD has been widely and successfully applied to environmental analyses of the air (Heavner et al., 1992; Hodgson, 1995; Massold et al., 2005) and soil (Zhao et al., 2019), potential applications in food control are still rather underexplored. In this field, TD started as a version of dynamic HS (Purge and Trap) used to enrich headspace extracts before GC analysis (Pillonel et al., 2002). When disconnected from Purge and Trap, it was sometimes called Direct Thermal Desorption (DTD). TD has several advantages over the HS methods referred to above: greater sensitivity compared to HS-SPME, the possibility of being directly coupled to GC (Esteban et al., 1996), the need for very small quantity of sample and the possibility to reanalyze the same extract several times (Göğüş et al., 2007). Not only it is appropriate for qualitative analysis because of its rapidity and simplicity, it is also suitable for quantitative analysis because carefully selected trapping sorbent tubes can retain and further desorb all the

target compounds present in the sampled gas (>99% desorption efficiency)(Bart, 2001). Moreover, the smaller number of extraction parameters requiring optimization (type of adsorbent, flow, purge cycles) and the greater robustness due to the steel equipment, make it more time saving, reproducible and durable when compared to HS-SPME techniques.

In a previous paper (Lee et al., 2020), an on-line sampling method for baking vapors using sorbent tubes coupled to GC-MS analysis was developed. It proved that TD-GC-MS was an appropriate and rapid technique to analyze a large number of volatile compounds with a wide range of physicochemical characteristics. The aim of the present work was to develop and optimize a quantitative approach for TD-GC-MS using in-tube calibration and isotope standard addition, with an application and validation for determining 10 process-induced compounds sampled on-line during the thermal transformation of a food model (baked model cake).

#### 2 Materials and Methods

#### 2.1 Ingredients and reagents

3-methylbutanal (> 99%), pyrazine ( $\geq$  99%), 2-methylpyrazine ( $\geq$  99%), 2,5-dimethylpyrazine ( $\geq$  99%), 2,6-dimethylpyrazine ( $\geq$  99%), furfural ( $\geq$  99%), furfuryl alcohol ( $\geq$  98%), 5-methylfurfural ( $\geq$  99%), 5-hydroxymethylfurfural ( $\geq$  99%), and d4-pyrazine ( $\geq$  98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetic acid ( $\geq$  96%), methanol ( $\geq$  99.9%), and ethanol ( $\geq$  95%) were purchased from Carlo Erba (Val de Reuil, France) and d4-furfural ( $\geq$  99.7%) was obtained from CIL Cluzeau, CDN Isotopes (Pointe-Claire, Canada). Table 1 summarizes the main characteristics of the volatile compounds selected for the study.

#### Table 1. Characteristics of the volatile compounds selected for the study

Compound	CAS No	log K <sub>ow</sub> <sup>a</sup>	Pv (mm Hg at 25°C) <sup>b</sup>	Selected ions (m/z) <sup>d</sup>
Analytes (A)				
3-methylbutanal	590-86-3	1.23	50	58, 71
Pyrazine	290-37-9	-0.2	10.81	53, 80
2-methylpyrazine	109-08-0	0.21	8.06	67, 94
2,5-dimethylpyrazine	123-32-0	0.63	3.18	42, 108
2,6-imethylpyrazine	108-50-9	0.54	4.57	42, <b>108</b>
Acetic acid	64-19-7	-0.17	15.7	60
Furfural	98-01-1	0.41	2.21	95, <b>96</b>
5-methylfurfural	620-02-0	0.67	0.610	81, 109, 110
Furfuryl alcohol	98-00-0	0.28	0.609	81, 97, 98
5-hydroxymethylfurfural	67-47-0	-0.6	$5.28 \times 10^{-3}$	97, <b>126</b>
Deuterated Internal standards (dIS)				
d4-pyrazine	1758-62-9	-0.2	41.6	56, 84
d4-furfural	1219803-80-1	0.4	n.d. <sup>c</sup>	99, <b>100</b>

<sup>a</sup>: octanol/water partition coefficients from Pubchem or EPI Suite<sup>TM</sup> v4.0 data bases

<sup>b</sup>: P<sub>V</sub>: Vapor pressure from Pubchem database

°: Not determined

<sup>d</sup>: Quantifier ions are in bold

n.d.: not determined

The ingredients used for the model sponge cakes were Ultrapure water, produced by an Integral 3 water purification system from Millipore<sup>®</sup>, native corn starch (Cargill, Wayzata, MN, USA) with a water content of 12.4% w/w (measured according to NF norm V05 707), and food grade cellulose derivatives (Dow Chemicals, Midland, MI, USA): methylcellulose (MC) type SGA7C and hydroxypropyl methyl cellulose (HPMC) type K250M. D-(+)-Glucose was supplied by Roquette Frères (Lestrem, France) and L-Leucine ( $\geq$  99%, Food Grade) was purchased from Sigma-Aldrich (St. Louis, MO,USA).

#### 2.2 Preparation of stock, working and calibration solutions

The stock methanolic solution of analytes contained 3-methylbutanal (260 mg.g<sup>-1</sup>), pyrazine (0.260 mg.g<sup>-1</sup>), 2-methylpyrazine (700 mg.g<sup>-1</sup>), 2,5-dimethlyprazine (0.680 mg.g<sup>-1</sup>), 2,6-dimethlyprazine (0.300 mg.g<sup>-1</sup>), acetic acid (26.0 mg.g<sup>-1</sup>), furfural (20.0 mg.g<sup>-1</sup>), 5-methlyfurfural (4.80 mg.g<sup>-1</sup>), furfuryl alcohol (2.10 mg.g<sup>-1</sup>) and 5-hydroxymethylfurfural (4.00 mg.g<sup>-1</sup>). The stock methanolic solution for the deuterated internal standards (*d*IS) contained d4-furfural and d4-pyrazine at a concentration of 2.55 mg.g<sup>-1</sup>. All stock solutions were stored at  $-20^{\circ}$ C for up to two months in hermetically sealed amber glass bottles.

The working solution of *d*IS d4-pyrazine and d4-furfural  $(8.00 \cdot 10^{-2} \text{ g.L}^{-1})$  was prepared by diluting a proper amount of stock *d*IS solution in methanol. Likewise, working solutions of analytes at five concentrations were obtained by diluting the stock solution in methanol. The concentration ranges were as follows: 0.316 to 32.5 g.L<sup>-1</sup> for 3-methylbutanal;  $3.94 \cdot 10^{-4}$  to  $0.123 \text{ g.L}^{-1}$  for pyrazine,  $1.09 \cdot 10^{-3}$  to  $0.400 \text{ g.L}^{-1}$  for

2-methylpyrazine,  $1.04 \cdot 10^{-3}$  to  $0.326 \text{ g.L}^{-1}$  for 2,5-dimethlyprazine,  $4.69 \cdot 10^{-4}$  to  $0.147 \text{ g.L}^{-1}$  for 2,6-dimethlyprazine, 0.038 to  $12.0 \text{ g.L}^{-1}$  for acetic acid, 0.030 to  $9.44 \text{ g.L}^{-1}$  for furfural,  $7.39 \cdot 10^{-3}$  to 2.31 g.L<sup>-1</sup> for 5-methylfurfural,  $3.26 \cdot 10^{-3}$  to  $1.02 \text{ g.L}^{-1}$  for furfuryl alcohol and  $6.10 \cdot 10^{-3}$  to  $1.91 \text{ g.L}^{-1}$  for 5-hydroxymethylfurfural. These concentrations were chosen to cover the peak areas found during baking of model cakes in a previous semi-quantitative study (Lee et al., 2020).

Calibration solutions containing a (constant) concentration of  $8.00 \cdot 10^{-2}$  g.L<sup>-1</sup> d4-pyrazine and d4-furfural and increasing concentrations of analytes were set at the same analyte concentration levels as previously mentioned.

The working and calibration solutions were stored at -20°C for up to one month in hermetically sealed amber glass bottles.

#### 2.3 Preparation and baking of the model cakes

A model cake was prepared according to the method described in Lee et al., (2020) using a hydrocolloid solution of HPMC and MC foamed with maize starch and enriched with glucose and leucine prior to baking. Twenty grams of batter were poured in disposable cylindrical aluminum molds (diameter = 6.6 cm, mold height = 4 cm, cake height = 1.3 cm) and a total of nine cakes were baked at the same time in an instrumented pilot oven with precise and uniform control of temperature (Bongard, Wolfisheim, France) (Fehaili et al., 2010). Baking trials were conducted in triplicate at  $170^{\circ}$ C and under a high level of convection.

#### 2.4 On-line sampling of baking vapors by sorbent tubes

Vapors were sampled during baking according to the method from Lee et al., (2020). An Air Toxics<sup>TM</sup> sorbent tube (Perkin Elmer, Waltham, MA, USA), selected for its capacity to trap C3-C12 volatile compounds, collected the internal atmosphere of the oven through a deactivated and silanized glass column (internal diameter = 4.5 mm, length = 18 cm) at a flow rate of 50 mL.min<sup>-1</sup> for 4 min by means of a VCP 130 vacuum pump (VWR, Radnor, PA, USA). The total volume of 200 mL of baking vapor was sufficient to meet the analytical limits. Prior to any experiments, precautions were taken to prevent external contamination: the oven was heated at 300°C for 1 hour under the same extraction flow and the glass column was rinsed with ethanol and dried carefully to eliminate any potential residues.

Baking vapors were sampled at three different times (2-6, 8-12, and 86-90 min) representing the very early and advanced stages of the process and considering that the amounts of the markers were increasing with time at 170°C (Lee et al., 2020). The sampling was conducted in triplicate.

A median time was then attributed to each sampling: 4, 10 and 88 min. After sampling, each sorbent tube was removed and spiked with 1  $\mu$ L of the deuterated standard solution (*d*IS) then sealed immediately with a Teflon<sup>®</sup> cap, stored at room temperature and analyzed within the day.

#### 2.5 Thermal desorption of sorbent tubes

Sorbent tubes were desorbed using an automated TurboMatrix 650 thermal desorber (Perkin Elmer, USA) adapting the method described by Lee et al., (2020). Firstly, a dry air purge at ambient temperature was applied for 10 min at 50 mL.min<sup>-1</sup> in order to remove any traces of water from the tube. The volatile compounds were then desorbed at 330°C for 20 min using helium as carrier gas at a flow rate of 60 mL.min<sup>-1</sup> and with an inlet split of 8 mL.min<sup>-1</sup>. The compounds were then cryo-focused on an Air Monitoring® cold trap (-20°C) then sent to the GC column by rapidly heating the trap to 330°C at 99°C.s<sup>-1</sup>, with a 15 mL.min<sup>-1</sup> outlet split. In this manner, 7.5% of the volatile compounds desorbed from the sorbent tube were transferred to the GC system at a constant gas flow rate of 1.4 mL.min<sup>-1</sup> *via* a transfer line heated at 270°C. After each injection, the trap was cleaned by setting the hold time to 45 min at 330°C and the sorbent tubes were systematically purged and conditioned with helium at a flow rate of 50 mL.min<sup>-1</sup> for 40 min at 330°C.

#### 2.6 GC-MS analysis and quantification of thermally desorbed volatile compounds

Volatile compounds were analyzed using a Trace 1300 Thermo Scientifc Gas Chromatograph (Waltham, MA, USA) equipped with a DB-Wax GC column (60 m  $\times$  0.25 mm  $\times$  0.5 µm; Agilent, Santa Clara, CA, USA) and coupled with a Thermo Scientific ISQ QD (Waltham, MA, USA) mass spectrometry detector. Helium was used as the carrier gas at a constant flow rate of 1.2 mL.min<sup>-1</sup>. The GC oven started at 100°C and the temperature was raised to 184°C by increments of 3°C.min<sup>-1</sup>, to 240°C by increments of 15°C.min<sup>-1</sup> and then held at that level for 11 min. MS transfer line and ion source temperatures were set at 270°C and 200°C, respectively. The ionization mode was electron impact (EI), 70 eV. Data were acquired in two segments including a full scan mode (from 25 to 250 m/z at 0.1 s per scan) and a selected ion monitoring (SIM) mode, with a dwell time of 0.2 s for each selected ion as shown in Table 1.

Compounds from baking extracts were identified by analyzing the pure standards, performing mass spectral matches with the Wiley 8 and NIST 08 mass spectra databases, and comparison with the Van der Dool retention indices measured on the DB-Wax column.

Chromatographic peak areas for each compound were calculated by extracting the quantifier ions from the SIM mode acquisition data using Quan Browser, Xcalibur 2.1.0 SP1, Build 1160 (Thermo Scientific, Waltham, MA, USA).

Calibration curves for each compound were built using the ratio of the chromatogram peak areas (analyte *vs d*IS) plotted against the corresponding concentration. d4-pyrazine was used for 3-methylbutanal, pyrazine, 2-methylpyrazine, 2,5-dimethylpyrazine and 2,6-dimethylpyrazine whereas d4-furfural was used for acetic acid, furfural, 5-methylfurfural, furfuryl alcohol and 5-hydroxymethylfurfural.

#### 2.7 Analytical strategy for development of the quantitative TD-GC-MS method

Figure 1 summarizes the global analytical strategy (calibration and sampling), including the parameters tested and the performance criteria chosen for optimization.



Figure 1: Analytical strategy applied for development of the quantitative TD-GC-MS method using in tube spiking: analytical steps are indicated in red for calibration and sampling tubes while the tested parameters and responses are in dark green on the side and the corresponding performance criteria chosen for optimization are in light green on the side.

Firstly, different desorption times (10, 20, 30 and 60 min) were compared. The tubes were analyzed twice and the quantity recovered from the first run was compared to the sum of those of first and second runs  $(recovery = Area_{1st run}/(Area_{1st run} + Area_{2nd run}))$ . It was concluded that 20 min was the most appropriate time, with average recoveries higher than 99.5% except for acetic acid (97.4%) and 5-HMF (91.1%) (n = 5; see supplementary data). Secondly, two spiking modes for introducing the analytes and the dIS into the tubes were compared. Liquid spiking consisted in the direct injection of 1  $\mu$ L of the working solution (calibration or analyte solution) into the top of the sorbent tube using an electronic eVOL XR 5 µL-precision syringe (SGE Analytical Science Europe Ltd, Milton Keynes, UK). Vapor spiking consisted in introducing the same amount (1  $\mu$ L) of working solution in a vaporized form by means of a GC injector port (300°C, constant helium flow rate 50 mL.min<sup>-1</sup>, splitless mode) connected to the sorbent tube *via* a deactived silica column (internal diameter = 0.25 mm, length = 25 cm,  $300^{\circ}$ C). The criterion of choice was the repeatability of spiking (RSD<sub>chromatographic response</sub> < 15% for all analytes and at all concentration levels). Any eventual breakthrough of this spiking mode was assessed by vapor spiking a solution of 3-methylbutanal, 2,5-dimethypyrazine, acetic acid, furfural, furfuryl alcohol and 5-hydroxymethylfurfural at the highest concentration level into two sorbent tubes in series and checking for any eventual carry-over into the second tube. The quantity recovered from the first tube was thus compared to the sum of those of first and second tubes (carry-over =  $\text{Area}_{2nd \text{ tube}}/(\text{Area}_{1st \text{ tube}} + \text{Area}_{2nd \text{ tube}})$ ). It was concluded that the overall breakthrough was negligible, with average carry-overs lower than 0.3% except for acetic acid (15.7%) and 5-HMF (5.0%) (n = 5; supplementary data).

Finally, the reliability of the in-tube *d*IS introduction method was assessed. Although the calibration tubes contained both the analytes (Ai) and the *d*IS, the sampling tubes (i.e. the sorbent tubes used for on-line extraction) always required a further addition of isotope standard (Figure 1). To achieve quantitation without any bias, it was evaluated whether there was any potential difference in the responses of the analytes and those of the *d*IS between calibration and sampling. In order to simulate vapor sampling, working solutions of analytes were spiked into the sorbent tubes. The *d*IS areas and A/*d*IS responses between the calibration and sampling tubes were compared using Tukey and Fisher tests (p > 0.05%).

#### 2.8 Performance evaluation

Linearity, *LOD*, *LOQ* and the matrix effect were evaluated according to Aszyk, Woźniak, Kubica, Kot-Wasik, & Wasik, 2019; Cepeda-Vázquez et al., 2016. The analytical blanks used to validate the method came from the empty oven atmosphere sampled under the same heating and extraction conditions as previously presented in section 2.4.

Linearity was assessed using four- or five-point calibration curves built in quadruplicate with the mean peak area ratio (Area<sub>analyte</sub>/Area<sub>dIS</sub>) of the blank (n = 6) used as the intercept. *LOD* and *LOQ* values for each analyte were determined using the mean peak area ratio (Area<sub>analyte</sub>/Area<sub>dIS</sub>) of blanks with a signal-to-noise ratio of 3 and 10, respectively.

The analytical blanks were spiked with the calibration solutions so a matrix-matched calibration was obtained. The sorbent tubes were spiked with calibration solutions so that the calibration curve was obtained. The matrix effect (%) was evaluated by comparing the slopes of these two curves according to Equation (1).

Matrix effect (%) = 
$$\left(\frac{Slope_{Matrix-matched calibration}}{Slope_{Calibration}} - 1\right) \times 100$$
 (1)

#### **3** Results and Discussion

#### **3.1** Spiking method for 10 volatile analytes over a broad range of concentrations

A robust, reliable and reproducible method to introduce calibration solutions into the sorbent tubes is of paramount importance in order to develop a quantitative method.

A previous study by Liaud, Nguyen, Nasreddine, & Le Calvé, (2014) had found liquid spiking to be more time-saving and easier to implement than vapor spiking because it does not require any solvent evaporation. However, this conclusion was reached when studied analytes (benzene, toluene, ethylbenzene, mbp-xylene and o-xylene) and the types of sorbent tubes used differed from those in the present study. On the other hand, vapor sampling may better mimic the conditions of on-line sampling applications. Therefore, in the present study, we compared the two spiking techniques over a range of 10 specific process-induced VOCs and a broad range of concentrations.

Table 2 shows the responses obtained for two sets of analytes using both methods.

Liquid spiking proved to be more repeatable than vapor spiking for 2,5-dimethylpyrazine, furfural, furfuryl alcohol and 5-hydroxymethylfurfural, and over the chosen range of concentrations. On the other hand, vapor spiking globally produced higher RSD whatever the level of concentration. This result could be explained by the larger number of sources of variability induced by the experimental device (gas flow, inlet and column temperature, injected volume, eventual leakage, etc.) when compared to liquid spiking which requires fewer steps. These results therefore confirmed the trends observed by Liaud, Nguyen, Nasreddine, & Le Calvé, (2014). Nevertheless, the results for 3-methylbutanal and acetic acid presented poorer repeatability for with both spiking techniques when low concentration levels where applied. This may be explained by the fact that the two compounds were the most volatile of the evaluated analytes (Table 1). Liquid spiking was therefore tested further on the second set of volatile analytes, i.e. key volatile markers for bakery products such as pyrazine, 2-methylpyrazine, 2,6-dimethylpyrazine and 5-methylfurfural. The results confirmed good repeatability, with RSD values lower than 15% for almost all the concentration levels for all compounds. The liquid spiking mode was therefore chosen for all subsequent analyses.

#### 3.2 Reliability of the in-tube spiking method for deuterated internal standards

As mentioned above, a further step was necessary for the sampling tubes, consisting in spiking the dIS solution just after trapping the volatile compounds from the gaseous phase (Figure 1).

	Liquid spiking					Vapor spiking				
Compound	Amount <sup>c</sup> (ng)	Response (Area <sub>analyte</sub> /Area <sub>dis</sub> )		RSD (%)	Amount <sup>c</sup> (ng)	Response (Area <sub>analyte</sub> /Area <sub>dis</sub> )			RSD (%)	
3-methylbutanal <sup>a</sup>	38	0.29	+	0.04	14	91	0.15	+	0.02	12
Sinceryibutanar	78	0.5	+	0.1	22	181	0.24	+	0.03	12
	400	2.3	+	0.3	11	923	1.12	+	0.07	
	1585	9.5	±	0.6	7	1841	2.06	±	0.05	2
2,5-dimethylpyrazine <sup>a</sup>	51	1.30	±	0.06	5	99	0.43	±	0.05	12
	104	2.85	±	0.02	1	197	0.72	±	0.05	6
	529	9.8	±	0.5	5	1003	3.3	±	0.1	3
	1053	16.2	±	1.2	7	2000	5.90	±	0.09	2
Acetic acid <sup>b</sup>	41	0.7	±	0.2	33	94	0.33	±	0.09	27
	84	1.3	±	0.2	15	187	0.43	±	0.09	20
	427	4.3	±	0.3	6	953	2.0	±	0.1	6
	1695	17.6	±	1.0	6	1901	4.3	±	0.2	6
Furfural <sup>b</sup>	43	1.49	±	0.03	2	95	0.6	±	0.1	19
	88	2.9	±	0.1	4	188	1.12	±	0.04	3
	446	12.7	±	0.7	5	956	5.04	±	0.01	0
	1768	42.1	±	1.1	3	1908	9.4	±	0.8	8
Furfuryl alcohol <sup>b</sup>	46	1.08	±	0.01	1	101	0.22	±	0.07	30
	94	2.30	±	0.09	4	202	0.41	±	0.07	16
	479	12.0	±	0.9	8	1029	2.0	±	0.1	7
	1901	43.7	±	1.5	4	2053	3.8	±	0.1	3
5-hydroxymethylfurfural <sup>b</sup>	79	0.77	±	0.07	10	90	0.2	±	0.1	68
	400	6.04	±	0.01	0.5	179	0.1	±	0.1	86
	795	11.3	±	0.8	7	914	0.4	±	0.1	31
	1585	33.9	±	1.1	3	1824	0.8	±	0.4	50
Pyrazine <sup>a</sup>	46	2.15	±	0.03	1	n.d.	n.	d.	n.d.	n.d.
	94	4.3	±	0.3	6	n.d.	n.	d.	n.d.	n.d.
	479	19.3	±	0.7	4	n.d.	n.	d.	n.d.	n.d.
	954	32.0	±	0.5	1	n.d.	n.	d.	n.d.	n.d.
2-methylpyrazine <sup>a</sup>	37	1.43	±	0.04	3	n.d.	n.	d.	n.d.	n.d.
	76	2.8	±	0.1	4	n.d.	n.	d.	n.d.	n.d.
	386	14.3	±	0.5	3	n.d.	n.	d.	n.d.	n.d.
	1530	52.32	±	10.1	19	n.d.	n.	d.	n.d.	n.d.
2,6-dimethylpyrazine <sup>a</sup>	39	1.70	±	0.08	4	n.d.	n.	d.	n.d.	n.d.
	79	3.2	±	0.2	6	n.d.	n.	d.	n.d.	n.d.
	400	16.0	±	0.5	3	n.d.	n.	d.	n.d.	n.d.
	795	28.3	±	1.5	5	n.d.	n.	d.	n.d.	n.d.
5-methylfurfural <sup>b</sup>	38	1.1	±	0.1	11	n.d.	n.	d.	n.d.	n.d.
	78	2.32	±	0.06	2	n.d.	n.	d.	n.d.	n.d.
	400	11.7	±	0.7	6	n.d.	n.	d.	n.d.	n.d.
	1585	44.3	±	1.6	4	n.d.	n.	d.	n.d.	n.d.

#### Table 2: Chromatographic responses of volatile analytes introduced into the sorbent tubes by liquid or vapor spiking

<sup>a</sup>: quantified using d4-pyrazine as *d*IS

<sup>b</sup>: quantified using d4-furfural as *d*IS

 $^{\text{c}:}$  amount corresponding to the injection of 1  $\mu\text{L}$  of working solution

n.d.: Not determined

Figure 2 shows the responses of the two *d*IS in both cases: calibration tubes where the analytes and *d*IS were present in the same solution so simultaneously spiked, and sampling tubes where the analytes were spiked first followed by the *d*IS in a second solution. The responses of d4-pyrazine and d4-furfural did not differ significantly for the calibration and sampling tubes (Tukey and Fisher tests, p > 0.05%), suggesting that the *d*IS were adsorbed in the same manner in both cases. Whether the *d*IS were introduced at the same time as the analytes or later did not alter their chromatographic responses.



Figure 2: Responses of dIS for simultaneous spiking in the calibration tubes and spiking after sampling in the sampling tubes (n = 5); the same letter for a same dIS means no significant difference (p < 0.05).

On the other hand, Table 3 highlights the responses for all the analytes evaluated at the three different concentration levels in the calibration and sampling tubes. Differences in (A/dIS) ratios were negligible in the majority of cases (70%) and no concentration dependency was detected. Therefore, the addition of the *d*IS did not remove the analytes that were already trapped. A notable discrepancy was seen regarding the acetic acid response at the highest concentration level. Due to the high repeatability of measurements, some minor differences were found for five other compounds, but in these cases no systematic bias was evident (no effect of the injection mode or level of concentration). We can reasonably conclude that spiking the *d*IS into a sampling tube already containing the analytes did not affect the response of most of the analytes whose responses were highly consistent with those found for the calibration tubes.

Finally, these results validate the in-tube spiking method for deuterated internal standards after the on-line sampling step.

Table 3. Responses of analytes with simultaneous spiking in the calibration tubes and spiking after sampling in the sampling tubes (n = 3)

		Response						
		$(Area_{analyte}/Area_{dIS})^* \pm SD$						
Compound	Amount (ng)	Calibration tubes			Sampling tubes			
3-methylbutanal	38	3 0.29 <sup>a</sup>	±	0.04	0.21 ª	±	0.03	
	78	3 0.5 ª	±	0.1	0.38 <sup>a</sup>	±	0.02	
	400	) 2.3 <sup>a</sup>	±	0.3	1.93 <sup>a</sup>	±	0.04	
2,5-dimethylpyrazine	5	1.30 ª	±	0.06	1.13 a	±	0.09	
	104	2.85 <sup>b</sup>	±	0.02	2.17 ª	±	0.08	
	529	9.8 ª	±	0.5	11.5 <sup>b</sup>	±	0.4	
Acetic acid	4	0.7 <sup>a</sup>	±	0.2	0.7 <sup>a</sup>	±	0.1	
	84	1.3 ª	±	0.2	1.5 <sup>b</sup>	±	0.2	
	42	4.3 <sup>b</sup>	±	0.3	2.58 ª	±	0.09	
Furfural	43	1.49ª	±	0.03	1.5 <sup>a</sup>	±	0.1	
	88	3 2.9 ª	±	0.1	2.68 ª	±	0.06	
	440	5 12.7 ª	±	0.7	12.6 ª	±	0.2	
Furfuryl alcohol	40	5 1.08 <sup>a</sup>	±	0.01	1.03 ª	±	0.05	
	94	2.30 <sup>b</sup>	±	0.09	2.0 ª	±	0.1	
	479	) 12.0 <sup>a</sup>	±	0.9	11.2 <sup>a</sup>	±	0.6	
5-hydroxymethylfurfural	79	0.77 <sup>a</sup>	±	0.07	0.8 ª	±	0.1	
	400	6.04 <sup>a</sup>	±	0.01	5.6 ª	±	1.0	
	79:	5 11.3 ª	±	0.8	14.0 ª	±	1.6	
Pyrazine	40	2.15 <sup>b</sup>	±	0.03	1.98 ª	±	0.05	
	94	4.3 <sup>b</sup>	±	0.3	3.88 ª	±	0.07	
	479	) 19.3 <sup>a</sup>	±	0.7	18.0 ª	±	0.4	
2-methylpyrazine	3'	1.43 ª	±	0.04	1.53 <sup>b</sup>	±	0.04	
	70	5 2.8 ª	±	0.1	2.87ª	±	0.08	
	380	5 14.3 <sup>a</sup>	±	0.5	14.3 <sup>a</sup>	±	0.5	
2,6-dimethylpyrazine	39	) 1.70 <sup>a</sup>	±	0.08	1.7 ª	±	0.1	
	79	) 3.2 <sup>a</sup>	±	0.2	3.28 <sup>a</sup>	±	0.11	
	400	) 15.9ª	±	0.5	16.4 ª	±	0.6	
5-methylfurfural	38	3 1.1 <sup>a</sup>	±	0.1	1.06 ª	±	0.06	
	78	3 2.32 <sup>b</sup>	±	0.06	2.1 <sup>a</sup>	±	0.1	
	400	) 11.7 <sup>a</sup>	±	0.7	11.5 <sup>a</sup>	±	0.7	

\*: Same letters in a row mean no significant difference (p < 0.05)

#### 3.3 Performance of the quantitative TD-GC-MS analysis

The performance characteristics of the TD-GC-MS method outlined above are summarized in Table 4.

	Linear regression					Linearity range	
Compound	Slope	Intercept*	R <sup>2</sup>	– Matrix effect (%)	LOD (ng)	LOQ (ng)	Upper limit (ng)
3-methylbutanal	0.0007	0.0175 ± 0.0008	0.9792	-4	3.5	11.5	32510
pyrazine	0.0125	0.007 ± 0.004	0.9950	0	0.97	3.25	123
2-methylpyrazine	0.0115	$0.0003 \pm 0.0001$	0.9930	1	0.025	0.085	340
2,5-dimethylpyrazine	0.0077	0.00010 ± 0.00003	0.9874	2	0.013	0.041	326
2,6-dimethylpyrazine	0.0096	0.004 ± 0.001	0.9909	13	0.21	0.67	27
acetic acid	0.0035	0.005 ± 0.003	0.9877	0	2.8	9.4	12014
furfural	0.0074	0.006 ± 0.004	0.9599	2	1.4	4.7	9439
5-methylfurfural	0.0231	$0.0015 \pm 0.0007$	0.9778	1	0.02	0.28	2312
furfuryl alcohol	0.0092	0.0012 ± 0.0009	0.9855	0	0.29	0.97	1901
5-hydroxymethylfurfural	0.0078	$0.0002 \pm 0.0001$	0.8880	22	0.05	0.14	1909

Table 4. Performance characteristics of TD-GC-MS determinations for 10 targ	rget analytes
---	---------------

\*: mean of the blanks' area ratio between the analyte and its assigned dIS

The ratios (A/*d*IS) of the analytical blanks were low (0.00010-0.0175). These values were used as intercepts. Good linearity was observed throughout the concentration range, and the linearity range was defined as that between LOQ and the upper concentration. LOD and LOQ were calculated in ng for the 10 analytes. LOQ ranged from 0.041 ng (2,5-dimethylpyrazine) to 11.5 ng (3-methylbutanal) which was very satisfactory. The data thus obtained were not very comparable to those found in the literature where LOD and LOQ were expressed as concentrations, but a comparison could be made for furfural: the present method produced an LOQ which was 10 times lower than that obtained using a TD-GC-MS/MS method developed for e-cigarette aerosol by Aszyk et al., (2019) ( $LOQ_{furfural} = 4.7$  ng and 19 g, respectively).

The pyrazine group displayed remarkably stable responses, explaining the excellent linearity observed ( $R^2$  within the range 0.9874-0.9950) and low *LOD* and *LOQ* (down to picogram levels). Acetic acid and furfurylic compounds also had very good linearity for very broad ranges of concentration.

Despite the fact that 5-hydroxymethylfurfural was the least volatile and most polar compound compared to the other analytes, a low LOQ (0.14 ng) was determined but with moderate linearity ( $R^2 = 0.8880$ ) and a matrix effect value higher than the threshold usually chosen for a significant matrix effect (+/- 20%).

Finally, for all the other analytes, no matrix effect was apparent, meaning that any suppression or enhancement of the signal due to the sample matrix could be disregarded. This method is therefore globally well suited to quantifying intense variations in the concentration of the pool of volatile markers that are likely to occur during an industrial process.

# **3.4** Application to analyzing process-induced volatile compounds in the baking vapors of a model cake

This quantitative TD-GC-MS method was then applied to the targeted analysis of 10 process-induced compounds released and sampled during a baking operation. A model food product (model cake) was used as described in Lee et al., (2020), to generate specific compounds issued from Maillard reaction and caramelization between one sugar and one amino acid, in order to study reaction mechanisms. These volatile compounds are linked to sensory, safety and quality in terms of aroma and potential toxicity (Birch et al., 2014; Cha et al., 2019; Crews & Castle, 2007).

In order to evaluate the suitability of the method to follow the progress of the thermal reactions throughout an entire baking process, the ten targeted analytes were analyzed at three different baking times which included a very early (4 min) and very late baking stage (88 min) thus producing very different concentrations. Having an on-line sample that lasts a known length of time at a given flow rate, it is possible to calculate the volume of gas passing through the tube, enabling expression of the concentration of each analyte present in the oven in ng.mL<sub>air</sub><sup>-1</sup> by hypothesizing that the air in the oven is perfectly stirred when the oven is at its highest convection rate. Considering the potentially wide range of duration of a cake baking (up to 60 min depending on the targeted intensities), it appears that a sampling duration of 4 min was short enough to obtain multiple different samples at all stages of the process, enabling a detailed description of the reaction dynamics.

Figure 3 groups the 10 process-induced compounds based on their chemical class and the concentrations found in the sampled vapors. It is worth noting that thanks to the high sensitivity of the TD-GC-MS method, it was possible to detect the compounds even at the earliest step of processing (at 4 min baking, meaning sampling from 2 to 6 min baking).

Pyrazine and substituted pyrazines (Figure 3A) are important process-induced compounds which play a major role in the aroma of baked foods (Grosch & Schieberle, 1997; Maire et al., 2013), even though they are found at trace quantities in the food matrices. TD-GC-MS enabled quantification of two of these strong odor-active compounds in the baking vapors, even after 4 min of baking, although at very low levels (6.88 ng for 2-methylpyrazine and 1.12 ng for 2,5-dimethylpyrazine). These trace compounds displayed a global increase during baking of up to 26.1 ng (corresponding to 0.13 ng.mL<sub>air</sub><sup>-1</sup>) for 2-methylpyrazine after 88 min of baking. These results were consistent with those obtained by Rega et al., (2009) using a real sponge cake; using on-line SPME-GC-MS analysis they showed that pyrazine levels increased in line with baking time.

Likewise, furanic compounds (furfural, 5-methylfurfural, furfuryl alcohol, and 5-hydroxymethylfurfural) increased significantly during baking (Figure 3B). These compounds were found in quite large amounts compared to pyrazines, particularly after a longer baking time, which was consistent with data on different cereal products (Ait Ameur et al., 2008; Petisca et al., 2013; Rega et al., 2009; Srivastava et al., 2018). Among these, furfural reached the highest concentration in the baking vapors (788 ng corresponding to 4 ng.mL<sub>air</sub><sup>-1</sup> at 88 min). These compounds could be closely followed for mitigation purposes (Capuano &

Fogliano, 2011; Rannou et al., 2016), so this highly sensitive method could be used for their early detection and quantification in both the atmosphere and food matrices during processing.

Figure 3: Process-induced volatile compound compounds were sampled on sorbent tubes fo Finally, the compounds found at the hi of Maillard or caramelization reactions corresponding to 46 ng.mL<sub>air</sub><sup>-1</sup>) after {

В

found at a very high level after only 4 corresponding to 48 ng.mL<sub>air</sub><sup>-1</sup>). This specific precursor (leucine) which react (Lee et al., 2020). Although both ac display different polarities. Nevertheles



a model cake. Volatile

to their different generation pathways d On-line sampling coupled to TD-GCappropriate method to monitor a broad generation and release behaviors durinş sensitive to be suitable for these types c Furthermore, the extraction technique including those derived from lipid oxi GC-MS (Lee et al., 2020). In the preser however, the developed method cou curves with their standards.

#### 4 Conclusion

During this work, an original and reliable TD-GC-MS method was developed for the quantitation of volatile compounds sampled on-line on sorbent tubes. For the first time, this method combines both in-tube calibration and deuterated standard addition. Ten volatile compounds that are likely to form during the heat processing of food were chosen as targeted analytes for their relevance with respect to food quality and for their different physicochemical properties. The key steps in the analytical procedure were optimized and carefully characterized in terms of recovery, repeatability and reliability.

The performance of the method was characterized over broad ranges of concentration. All analytes could be quantified with high sensitivity (LOQ at ng level), making it possible to express the concentrations in ng.mL<sup>-1</sup> of air. Quantitative TD-GC-MS with isotope standard addition therefore stands out as accurate and competitive when compared to existing methods for on-line applications.

This method was successfully applied to the on-line analysis of newly formed compounds during the baking of a model cake. For this application, reproducible results were found for the target analytes within very broad ranges of concentration between 0.15 ng and 0.63 ng, at three different baking times.

The high extraction capacity and robustness of the sampling method are a clear advantage compared to other extraction techniques previously used for on-line sampling such as SPME. This advantage, combined with the good linearity and high sensitivity of the method, means that quantitative TD-GC-MS is highly appropriate for the on-line extraction throughout a unit operation such as baking and could be relevant for food analysis applications such as the multi-residue analysis of volatile compounds linked to quality and safety as well as to reaction kinetics for multi-response modeling.

The quantitative approach presented here is transferable to determining other volatile markers (e.g. aldehydes, VOCs, furans) during other industrial or domestic processes (e.g. frying, drying) and in other types of food or emerging non-food applications.

#### Funding

This work was supported by a grant from ABIES doctoral school (Paris-Saclay University).

#### **Conflict of interest**

The authors have declared no conflict of interest.

#### **Bibliography**

- Ait Ameur, L., Rega, B., Giampaoli, P., Trystram, G., & Birlouez-Aragon, I. (2008). The fate of furfurals and other volatile markers during the baking process of a model cookie. *Food Chemistry*, 111(3), 758– 763. https://doi.org/10.1016/j.foodchem.2007.12.062
- Aszyk, J., Woźniak, M. K., Kubica, P., Kot-Wasik, A., & Wasik, A. (2019). Concentration levels of selected analytes in the gas phase of an e-cigarette aerosol. *Microchemical Journal*, 148, 717–724.

https://doi.org/10.1016/J.MICROC.2019.05.052

- Bart, J. C. (2001). Direct solid sampling methods for gas chromatographic analysis of polymer/additive formulations. *Polymer Testing*, 20(7), 729–740. https://doi.org/10.1016/S0142-9418(01)00027-7
- Birch, A. N., Petersen, M. A., & Hansen, Å. S. (2014). REVIEW: Aroma of Wheat Bread Crumb. *Cereal Chemistry Journal*, *91*(2), 105–114. https://doi.org/10.1094/CCHEM-06-13-0121-RW
- Capuano, E., & Fogliano, V. (2011). Acrylamide and 5-hydroxymethylfurfural (HMF): A review on metabolism, toxicity, occurrence in food and mitigation strategies. *LWT - Food Science and Technology*, 44(4), 793–810. https://doi.org/10.1016/j.lwt.2010.11.002
- Cepeda-Vázquez, M., Blumenthal, D., Camel, V., & Rega, B. (2016). Multivariate optimization of headspace trap for furan and furfural simultaneous determination in sponge cake. *Talanta*. https://doi.org/10.1016/j.talanta.2016.10.073
- Cepeda-Vázquez, M., Camel, V., Blumenthal, D., & Rega, B. (2019). Quality-driven design of sponge cake: Insights into reactivity, furan mitigation and consumer liking. *Food Chemistry*, 285, 94–103. https://doi.org/10.1016/J.FOODCHEM.2019.01.118
- Cepeda-Vázquez, M., Rega, B., Descharles, N., & Camel, V. (2018). How ingredients influence furan and aroma generation in sponge cake. *Food Chemistry*, 245, 1025–1033. https://doi.org/10.1016/J.FOODCHEM.2017.11.069
- Cha, J., Debnath, T., & Lee, K.-G. (2019). Analysis of α-dicarbonyl compounds and volatiles formed in Maillard reaction model systems. *Scientific Reports*, 9(1), 5325. https://doi.org/10.1038/s41598-019-41824-8
- Cho, I. H., & Peterson, D. G. (2010). Chemistry of bread aroma: A review. *Food Science and Biotechnology*, 19(3), 575–582. https://doi.org/10.1007/s10068-010-0081-3
- Crews, C., & Castle, L. (2007). A review of the occurrence, formation and analysis of furan in heatprocessed foods. *Trends in Food Science & Technology*, 18(7), 365–372. https://doi.org/10.1016/J.TIFS.2007.03.006
- Elmore, J. S. (2015). Aroma extract analysis. *Flavour Development, Analysis and Perception in Food and Beverages*, 47–61. https://doi.org/10.1016/B978-1-78242-103-0.00003-5
- Esteban, J. L., Martínez-Castro, I., Morales, R., Fabrellas, B., & Sanz, J. (1996). Rapid identification of volatile compounds in aromatic plants by automatic thermal desorption — GC-MS. *Chromatographia*, 43(1–2), 63–72. https://doi.org/10.1007/BF02272823
- Fehaili, S., Courel, M., Rega, B., & Giampaoli, P. (2010). An instrumented oven for the monitoring of thermal reactions during the baking of sponge cake. *Journal of Food Engineering*, 101(3), 253–263. https://doi.org/10.1016/J.JFOODENG.2010.07.003
- Göğüş, F., Özel, M. Z., & Lewis, A. C. (2007). The effect of various drying techniques on apricot volatiles analysed using direct thermal desorption-GC–TOF/MS. *Talanta*, 73(2), 321–325. https://doi.org/10.1016/J.TALANTA.2007.03.048
- Grosch, W., & Schieberle, P. (1997). Flavor of Cereal Products-A Review. Cereal Chemistry Journal,

74(2), 91-97. https://doi.org/10.1094/CCHEM.1997.74.2.91

- Hansen, A., & Schieberle, P. (2005). Generation of aroma compounds during sourdough fermentation: applied and fundamental aspects. *Trends in Food Science & Technology*, *16*(1–3), 85–94. https://doi.org/10.1016/J.TIFS.2004.03.007
- Heavner, D. L., Ogden, M. W., & Nelson, P. R. (1992). Multisorbent thermal desorption/gas chromatography/mass selective detection method for the determination of target volatile organic compounds in indoor air. *Environmental Science & Technology*, 26(9), 1737–1746. https://doi.org/10.1021/es00033a004
- Hodgson, A. T. (1995). A Review and a Limited Comparison of Methods for Measuring Total Volatile Organic Compounds in Indoor Air. *Indoor Air*, 5(4), 247–257. https://doi.org/10.1111/j.1600-0668.1995.00004.x
- Lee, J., Bousquières, J., Descharles, N., Roux, S., Michon, C., Rega, B., & Bonazzi, C. (2020). Potential of model cakes to study reaction kinetics through the dynamic on-line extraction of volatile markers and TD-GC-MS analysis. *Food Research International*, 132, 109087. https://doi.org/10.1016/J.FOODRES.2020.109087
- Liaud, C., Nguyen, N. T., Nasreddine, R., & Le Calvé, S. (2014). Experimental performances study of a transportable GC-PID and two thermo-desorption based methods coupled to FID and MS detection to assess BTEX exposure at sub-ppb level in air. *Talanta*, 127, 33–42. https://doi.org/10.1016/J.TALANTA.2014.04.001
- Maire, M., Rega, B., Cuvelier, M.-E., Soto, P., & Giampaoli, P. (2013). Lipid oxidation in baked products: Impact of formula and process on the generation of volatile compounds. *Food Chemistry*, 141(4), 3510–3518. https://doi.org/10.1016/j.foodchem.2013.06.039
- Massold, E., Bähr, C., Salthammer, T., & Brown, S. K. (2005). Determination of VOC and TVOC in Air Using Thermal Desorption GC-MS – Practical Implications for Test Chamber Experiments. *Chromatographia*, 62(1–2), 75–85. https://doi.org/10.1365/s10337-005-0582-z
- Moreira, N., Araújo, A. M., Rogerson, F., Vasconcelos, I., Freitas, V. De, & Pinho, P. G. de. (2019).
  Development and optimization of a HS-SPME-GC-MS methodology to quantify volatile carbonyl compounds in Port wines. *Food Chemistry*, 270, 518–526. https://doi.org/10.1016/J.FOODCHEM.2018.07.093
- Ozolina, V., Kunkulberga, D., Cieslak, B., & Obiedzinski, M. (2011). Furan derivatives dynamic in rye bread processing. *Procedia Food Science*, *1*, 1158–1164. https://doi.org/10.1016/J.PROFOO.2011.09.173
- Paik, J. S., & Venables, A. C. (1991). Analysis of packaged orange juice volatiles using headspace gas chromatography. *Journal of Chromatography A*, 540, 456–463. https://doi.org/10.1016/S0021-9673(01)88838-5
- Parker, J. K. (2013). The kinetics of thermal generation of flavour. *Journal of the Science of Food and Agriculture*, 93(2), 197–208. https://doi.org/10.1002/jsfa.5943

- Petisca, C., Henriques, A. R., Pérez-Palacios, T., Pinho, O., & Ferreira, I. M. P. L. V. O. (2013). Study of hydroxymethylfurfural and furfural formation in cakes during baking in different ovens, using a validated multiple-stage extraction-based analytical method. *Food Chemistry*, 141(4), 3349–3356. https://doi.org/http://dx.doi.org/10.1016/j.foodchem.2013.05.128
- Pico, J., Antolín, B., Román, L., Gómez, M., & Bernal, J. (2018). Analysis of volatile compounds in glutenfree bread crusts with an optimised and validated SPME-GC/QTOF methodology. *Food Research International*, 106, 686–695. https://doi.org/10.1016/J.FOODRES.2018.01.048
- Pico, J., Tapia, J., Bernal, J., & Gómez, M. (2018). Comparison of different extraction methodologies for the analysis of volatile compounds in gluten-free flours and corn starch by GC/QTOF. *Food Chemistry*, 267, 303–312. https://doi.org/10.1016/J.FOODCHEM.2017.06.157
- Pillonel, L., Bosset, J. ., & Tabacchi, R. (2002). Rapid Preconcentration and Enrichment Techniques for the Analysis of Food Volatile. A Review. LWT - Food Science and Technology, 35(1), 1–14. https://doi.org/10.1006/FSTL.2001.0804
- Poinot, P., Arvisenet, G., Grua-Priol, J., Fillonneau, C., Le-Bail, A., & Prost, C. (2010). Influence of inulin on bread: Kinetics and physico-chemical indicators of the formation of volatile compounds during baking. *Food Chemistry*, *119*(4), 1474–1484. https://doi.org/http://dx.doi.org/10.1016/j.foodchem.2009.09.029
- Pozo-Bayón, M.A., Guichard, E., & Cayot, N. (2006). Flavor Control in Baked Cereal Products. Food Reviews International, 22(4), 335–379. https://doi.org/10.1080/87559120600864829
- Pozo-Bayón, Maria Angeles, Ruíz-Rodríguez, A., Pernin, K., & Cayot, N. (2007). Influence of eggs on the aroma composition of a sponge cake and on the aroma release in model studies on flavored sponge cakes. *Journal of Agricultural and Food Chemistry*, 55(4), 1418–1426. https://doi.org/10.1021/jf062203y
- Rannou, C., Laroque, D., Renault, E., Prost, C., & Sérot, T. (2016). Mitigation strategies of acrylamide, furans, heterocyclic amines and browning during the Maillard reaction in foods. *Food Research International*, 90, 154–176. https://doi.org/10.1016/j.foodres.2016.10.037
- Rega, B., Fournier, N., & Guichard, E. (2003). Solid Phase Microextraction (SPME) of Orange Juice Flavor: Odor Representativeness by Direct Gas Chromatography Olfactometry (D-GC-O). https://doi.org/10.1021/JF034384Z
- Rega, B., Guerard, A., Delarue, J., Maire, M., & Giampaoli, P. (2009). On-line dynamic HS-SPME for monitoring endogenous aroma compounds released during the baking of a model cake. *Food Chemistry*, 112(1), 9–17. https://doi.org/10.1016/j.foodchem.2008.05.028
- Salim-ur-Rehman, Paterson, A., & Piggott, J. R. (2006). Flavour in sourdough breads: a review. Trends in Food Science & Technology, 17(10), 557–566. https://doi.org/10.1016/J.TIFS.2006.03.006
- Sgorbini, B., Cagliero, C., Liberto, E., Rubiolo, P., Bicchi, C., & Cordero, C. (2019). Strategies for Accurate Quantitation of Volatiles from Foods and Plant-Origin Materials: A Challenging Task. *Journal of Agricultural and Food Chemistry*. https://doi.org/10.1021/acs.jafc.8b06601

- Srivastava, R., Bousquières, J., Cepeda-Vázquez, M., Roux, S., Bonazzi, C., & Rega, B. (2018). Kinetic study of furan and furfural generation during baking of cake models. *Food Chemistry*, 267, 329–336. https://doi.org/10.1016/j.foodchem.2017.06.126
- van Boekel, M. A. J. S. (2001). Kinetic aspects of the Maillard reaction: a critical review. *Nahrung/Food*, 45(3), 150–159. https://doi.org/10.1002/1521-3803(20010601)45:3<150::AID-FOOD150>3.0.CO;2-9
- Xu, C.-H., Chen, G.-S., Xiong, Z.-H., Fan, Y.-X., Wang, X.-C., & Liu, Y. (2016). Applications of solidphase microextraction in food analysis. *TrAC Trends in Analytical Chemistry*, 80, 12–29. https://doi.org/10.1016/J.TRAC.2016.02.022
- Zanin, R. C., Smrke, S., Kurozawa, L. E., Yamashita, F., & Yeretzian, C. (2020). Novel experimental approach to study aroma release upon reconstitution of instant coffee products. *Food Chemistry*, 317, 126455. https://doi.org/10.1016/J.FOODCHEM.2020.126455
- Zhang, Y., Yang, N., Fray, R. G., Fisk, I., Liu, C., Li, H., & Han, Y. (2018). Characterization of volatile aroma compounds after in-vial cooking of foxtail millet porridge with gas chromatography-mass spectrometry. *Journal of Cereal Science*, 82, 8–15. https://doi.org/10.1016/J.JCS.2018.05.003
- Zhao, C., Dong, Y., Feng, Y., Li, Y., & Dong, Y. (2019). Thermal desorption for remediation of contaminated soil: A review. *Chemosphere*, 221, 841–855. https://doi.org/10.1016/j.chemosphere.2019.01.079
- Zhou, M., Robards, K., Glennie-Holmes, M., & Helliwell, S. (1999). *Analysis of Volatile Compounds and Their Contribution to Flavor in Cereals*. https://doi.org/10.1021/JF990428L