



# Improvement of a headspace solid phase microextraction-gas chromatography/mass spectrometry method for the analysis of wheat bread volatile compounds



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## ABSTRACT

An improved method based on headspace solid phase microextraction combined with gas chromatography–mass spectrometry (HS-SPME/GC-MS) was proposed for the semi-quantitative determination of wheat bread volatile compounds isolated from both whole slice and crust samples. A DVB/CAR/PDMS fibre was used to extract volatiles from the headspace of a bread powdered sample dispersed in a sodium chloride (20%) aqueous solution and kept for 60 min at 50 °C under controlled stirring. Thirty-nine out of all the extracted volatiles were fully identified, whereas for 95 other volatiles a tentative identification was proposed, to give a complete as possible profile of wheat bread volatile compounds. The use of an array of ten structurally and physicochemically similar internal standards allowed to markedly improve method precision with respect to previous HS-SPME/GC-MS methods for bread volatiles. Good linearity of the method was verified for a selection of volatiles from several chemical groups by calibration with matrix-matched extraction solutions. This simple, rapid, precise and sensitive method could represent a valuable tool to obtain semi-quantitative information when investigating the influence of technological factors on volatiles formation in wheat bread and other bakery products.

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## 1. Introduction

The pleasant smell of fresh wheat bread is one of the most important factors contributing to its consumer acceptance. More than 500 wheat bread volatile compounds have been reported in the literature, belonging to different chemical classes such as alcohols, aldehydes, ketones, pyrazines and other *N*-heterocycles, acids, furans, esters, sulphides and others [1,2]. They are mainly formed during the bread making process, through enzymatic activities and fermentation by yeasts and lactic bacteria before baking, and through Maillard and caramelisation reactions during baking [3]. During baking different temperatures are reached in the inner and the outer part of the dough and thermal induced processes by which volatiles are formed at this stage proceed to a different extent in the two parts of the dough. As a result, a markedly different volatile profile is produced in the crumb and the crust [3]. While only a couple of dozens of these volatiles have been recognised as

key players imparting the typical aroma of wheat bread crumb and crust [1,3–5], a larger range of volatile compounds may be worth of investigation as potential markers of chemical processes occurring during bread making or because they may contribute to the perceived aroma through their interactions with the recognised most potent bread odorants.

Several isolation techniques have been proposed for the analysis of wheat bread volatiles. The most effective approach in terms of limits of detection and trueness is that based on solvent extraction and high vacuum distillation, combined with stable isotope dilution assay for the GC-MS analysis [4,5]. This method, which allows for an exhaustive extraction of volatiles from the food matrix, provides quantitative information on their concentration in the bread sample, but it is quite labour intensive, complex, high time and solvent consuming. In many studies the headspace of wheat bread has been analysed by purge and trap techniques [6–9]: by these more simple methods it is possible to obtain information on a relatively complete profile of the bread volatile fraction, but differently from the above wet method, this information is only semi-quantitative in nature. The other common approach used in the last decade is also a semi-quantitative one and is based on the headspace analysis by

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the solid phase microextraction (HS-SPME) technique, combined, similarly to the other approaches, with gas chromatography–mass spectrometry [10–15]. In the same field of microextraction techniques, a single application of the headspace sorptive extraction technique has also been proposed [16].

SPME has recently become one of the most widely applied isolation technique in the analysis of food volatile compounds by virtue of simple and fast sample preparation, high sensitivity and enrichment factor, possibility of automation and minimal or no use of solvent [17,18]. However, in the majority of cases, SPME has been used only for qualitative rather than quantitative purposes, mainly due to the difficulties in quantification arising from the complex volatile compounds–matrix interactions. In addition, only a relatively small number of applications have been developed for solid foods [17]. In previous applications of HS-SPME to the analysis of wheat bread volatile compounds a rather incomplete profile has been generally detected, neglecting several important bread odorants [10,12–15]. Moreover, only in few cases information on method performance characteristics has been reported, and a poor precision in the determination of some important odorants has been observed [10–15].

The aim of this study was to improve previous HS-SPME/GC–MS methods for the analysis of wheat bread volatiles by providing a more complete profile of the volatile fraction, by enhancing method precision through the use of an array of structurally and physicochemically similar internal standards, and by giving a more complete description of method performance characteristics.

## 2. Experimental

### 2.1. Reagents and materials

All pure volatile compounds and tested internal standards, their CAS no. and purity, were reported in Table 1. Citric acid monohydrate was of >99.0% purity, whereas NaCl was of analytical grade. All of these reagents, along with a standard solution of C7–C30 saturated alkanes in hexane for retention indices determination, were purchased from Sigma-Aldrich Italy (Milan, Italy). Methanol used for preparation of volatile compounds stock solutions was of HPLC grade (Carlo Erba Reagents, Milan, Italy). All volatile pure compounds and internal standards stock solutions were prepared by dissolving about 10–100 mg of each component in 10 mL of methanol and stored at –20 °C.

The SPME holder for manual sampling and fibres were purchased from Supelco (Sigma-Aldrich Italy). Two types of fibres were used: a 50/30 µm divinylbenzene/carboxen/poly(dimethylsiloxane) (DVB/CAR/PDMS) fibre, and a 85 µm carboxen/poly(dimethylsiloxane) (CAR/PDMS) fibre. All fibres were conditioned as recommended by the manufacturer before the first use.

### 2.2. Bread loaves preparation and sampling

Samples of bread (2 loaves) were prepared according to the International Association for Cereal Science and Technology standard method for test baking of wheat flours, namely ICC method no. 131 [19]. A dough was made from a commercial wheat flour, water, compressed yeast, salt, sucrose and malt flour. Two steps of leavening, of 30 and 75 min, respectively, were carried out followed by baking in a ventilated oven at 220 °C for 30 min. Bread loaves were cooled at room temperature for 1 h and then cut in slices. At this point two distinct bread samples were prepared: whole slice samples, by collecting whole slices, and crust samples, by cutting crosswise a bread slice and collecting 1 cm of its outer

**Table 1**

List of pure volatile compounds and tested internal standards used in the study, their CAS no. and purity (%).

| Compound name                     | CAS no.                 | Purity (%)        |
|-----------------------------------|-------------------------|-------------------|
| <b>Aldehydes</b>                  |                         |                   |
| 2-Methyl butanal                  | 96-17-3                 | 98                |
| 3-Methyl butanal                  | 590-86-3                | ≥97               |
| Hexanal                           | 66-25-1                 | 98                |
| (E)-2-hexenal                     | 6728-26-3               | 98                |
| Methional                         | 3268-49-3               | 98                |
| Benzaldehyde                      | 100-52-7                | ≥99               |
| (E)-2-nonenal                     | 18829-56-6              | 97                |
| (E,Z)-2,6-nonadienal              | 557-48-2                | 95                |
| Phenylacetaldehyde                | 122-78-1                | ≥99               |
| (E,E)-2,4-decadienal              | 25152-84-5              | ≥97.0             |
| <b>Ketones</b>                    |                         |                   |
| Acetone                           | 67-64-1                 | ≥99.9             |
| 2,3-Butanedione                   | 431-03-8                | ≥99.0             |
| 1-Octen-3-one                     | 4312-99-6               | 96                |
| 6-Methyl-5-hepten-2-one           | 110-93-0                | 99                |
| <b>Esters</b>                     |                         |                   |
| Ethyl acetate                     | 141-78-6                | 99.8              |
| γ-Nonalactone                     | 104-61-0                | ≥98               |
| <b>Alcohols</b>                   |                         |                   |
| Ethanol                           | 64-17-5                 | ≥99.8             |
| 2-Methyl-1-butanol                | 137-32-6                | ≥99               |
| 1-Hexanol                         | 111-27-3                | ≥99               |
| 1-Octen-3-ol                      | 3391-86-4               | ≥98               |
| 1-Octanol                         | 111-87-5                | ≥99               |
| 2-Phenyl-1-ethanol                | 60-12-8                 | ≥99.0             |
| p-Vinyl guaiacol                  | 7786-61-0               | ≥98.0             |
| <b>Furans</b>                     |                         |                   |
| 2-Pentyl furan                    | 3777-69-3               | ≥98               |
| 2-Furfural                        | 98-01-1                 | 99                |
| 2-Acetyl furan                    | 1192-62-7               | ≥99               |
| 5-Methyl-2-furfural               | 620-02-0                | ≥98.5             |
| <b>Pyrazines</b>                  |                         |                   |
| 2,5-Dimethyl pyrazine             | 123-32-0                | ≥98.5             |
| 3-Ethyl-2,5-dimethyl pyrazine     | 27043-05-6 <sup>a</sup> | 96.5 <sup>a</sup> |
| 2-Ethyl-3,5-dimethyl pyrazine     | 27043-05-6 <sup>a</sup> | 96.5 <sup>a</sup> |
| <b>Pyroles, Pyridines</b>         |                         |                   |
| 1-Methyl pyrrole                  | 96-54-8                 | ≥99               |
| 2-Acetyl pyridine                 | 1122-62-9               | ≥99               |
| 2-Acetyl-1-methyl pyrrole         | 932-16-1                | ≥98               |
| 1-Furfuryl pyrrole                | 1438-94-4               | 99                |
| 2-Acetyl pyrrole                  | 1072-83-9               | ≥98.5             |
| <b>Sulphides</b>                  |                         |                   |
| Dimethyl disulphide               | 624-92-0                | ≥99.0             |
| Dimethyl trisulphide              | 3658-80-8               | ≥98               |
| <b>Carboxylic acids</b>           |                         |                   |
| Acetic acid                       | 64-19-7                 | ≥99.7             |
| <b>Hydrocarbons</b>               |                         |                   |
| Toluene                           | 108-88-3                | 99.8              |
| <b>List of internal standards</b> |                         |                   |
| 2,2-Dimethyl butanal              | 2094-75-9               | n.a. <sup>b</sup> |
| 3,3-Dimethyl butanal              | 2987-16-8               | 95                |
| 2-Ethyl butanal                   | 97-96-1                 | ≥92               |
| 2-Ethyl-2-butenal                 | 63883-69-2              | n.a. <sup>b</sup> |
| 4-Methyl-2-pentanal               | 108-11-2                | 98                |
| Diethyl disulfide                 | 110-81-6                | 99                |
| 3-Octen-2-one                     | 18402-82-9              | ≥98               |
| 1-(2-Furyl)-acetone               | 6975-60-6               | n.a. <sup>b</sup> |
| cis-7-Decen-1-al                  | 21661-97-2              | 96                |
| 5-Isobutyl-2,3-dimethyl pyrazine  | 54410-83-2              | 97                |
| p-Tolualdehyde                    | 104-87-0                | ≥97               |
| 2-Ethyl butyric acid              | 88-09-5                 | 99                |
| 1-Phenyl-2-propanol               | 698-87-3                | 98                |
| 3-Acetyl pyridine                 | 350-03-8                | ≥98               |

<sup>a</sup> The commercial standard is formed by the mixture of the two isomers. The percentage of the two isomers in the mixture has been determined by GC analysis.

<sup>b</sup> Information on purity was not provided by the supplier.

part. Then, about 60 g of whole slice sample and 30 g of crust sample, were frozen with liquid nitrogen and grounded by a laboratory grinding device (Ika, Staufen, Germany) to give a powder that was stored at –70 °C until analyses.

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