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Review article

Analytical methods for volatile compounds in wheat bread

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ABSTRACT

Bread aroma is one of the main requirements for its acceptance by consumers, since it is one of the first attributes perceived. Sensory analysis, crucial to be correlated with human perception, presents limitations and needs to be complemented with instrumental analysis. Gas chromatography coupled to mass spectrometry is usually selected as the technique to determine bread volatile compounds, although proton-transfer reaction mass spectrometry begins also to be used to monitor aroma processes. Solvent extraction, supercritical fluid extraction and headspace analysis are the main options for the sample treatment. The present review focuses on the different sample treatments and instrumental alternatives reported in the literature to analyse volatile compounds in wheat bread, providing advantages and limitations. Usual parameters employed in these analytical methods are also described.

Contents

Abbreviations: AEDA, Aroma Extraction Dilution Assay; CAR, Arboxen; CW, Arbowax; DHE, Dynamic Headspace Extraction; DVB, Divinylbencene; FD, Flavour Dilution Factor; FID, Flame Ionisation Detector; FTIR, Fourier Transformed Infrared Spectroscopy; GC, Gas Chromatography; GC × GC, Comprehensive Gas Chromatography; GC-O, Gas Chromatography-Olfactometry; HS, Headspace; IR, Infrared Spectroscopy; IS, Internal Standard; MS, Mass Spectrometry; MHE, Multiple Headspace Extraction; OAV, OdourActivity Value; PDMS, Polydimethylsiloxane; PEG, PolyethyleneGlycol; PTR-MS, Proton-Transfer Reaction Mass Spectrometry; RAS, Retronasal Aroma Simulator; RSD, Relative Standard Deviation; SAFE, Solvent Assisted Flavour Evaporation; SDE, Simultaneous Steam Distillation Extraction; SFE, Supercritical Fluid Extraction; SHS, Static Headspace; SIDA, Stable Isotope Dilution Assay; SPME, Solid Phase Micro Extraction; VS, Vacuum Sublimation.

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1. Introduction

Bread is one of the nourishments most consumed around the world and is considered as a basic foodstuff. Among the different properties of bread, odour quality is one of the most important since it is one of the first attributes perceived by consumers. Good bread should smell nice. The aroma of bread is composed by a large list of volatile compounds, including alcohols, aldehydes, esters, ethers, ketones, acids, hydrocarbons, pyrazines, pyrrolines, furans, lactones or sulphur compounds [1,2]. A volatile compound's profile depends on many factors such as the recipe [3], the use of sourdough [4], the type of fermentation [5], the addition of enzymes [6] and improvers [7] and the baking stage [8]. Storage also affects the aroma [9]. Modifications of the bread-making process and recipe lead to changes in the odour quality [1].

Although applied sensory strategies for evaluating the quality of consumer goods have been extensive in the food and beverage industry [10], there is very little information relating to the aromatic profile in the sensorial evaluation of bread [11]. Quality control normally relies on instrumental techniques, since there are difficulties inherent in the availability of sensory methods. There are logistical difficulties in setting up sensory panels in small companies, troubles collecting an adequate number of trained panellists, lack of reproducibility from sensory panels over long time periods and problems because of the high throughput screening sometimes necessary [10]. Instrumental techniques are more appropriated when evaluations are repetitive and fatiguing. However, instrumental techniques are never going to mimic human perception in order to know if the aroma of bread is pleasant. In an attempt to simulate the principles of smelling, electronic nose systems with different sensors have been developed. However, electronic noses have problems with selectivity (detectors are not universal) and with the possible lack of correlation with the properties of the sample [12].

Sometimes in sensorial analysis experts do not find significant differences between breads that are slightly different. However, analytical techniques are able to provide profiles of volatile compounds that discriminate these small but important differences [11]. Therefore, instrumental and sensory methods should be employed in a complementary way. In both cases, the whole bread could be analysed or only the crumb or crust.

Gas chromatography (GC) has usually been selected as the analytical technique employed to determine volatile compounds, both with the mass spectrometric (MS) or the flame ionisation (FID) detector [13]. For complicated aroma mixtures, when the separation power of single-dimensional chromatography is insufficient, two-dimensional GC (2D-GC or GC × GC) could be required [14], although there are only a few recent publications related to the use of GC × GC in the bread aroma field. On the other hand, proton-transfer reaction mass spectrometry (PTR-MS) has relatively late been employed as analytical technique in the analysis of bread aroma [15,16], with the aim of monitoring the generation of volatile compounds in processes such as fermentation or baking.

In the chemical analysis of bread aroma, there have emerged different options about the sample treatment, namely solvent extraction methods, supercritical fluid extraction (SFE) methods and the headspace (HS) analysis. Solvent extraction methods normally implied a Soxhlet extraction with organic solvents, followed by a distillation of the volatile fraction by different methods and a final concentration step with a Vigreux column. Those distillation methods have been employed in solvent extraction in order to isolate volatile compounds from non-volatile compounds, SAFE (Solvent Assisted Flavour Evaporation) being the most applied. SFE extractions are environmentally friendly methods where the extractant is a mixture of carbon dioxide with a little percentage of an organic modifier. On the other hand, HS methodologies implied the analysis of the gaseous phase formed above the solid phase when bread is heated. There have arisen three options: static HS (SHS), dynamic HS (DHE) and the most preferred HS-solid-phase microextraction (HS-SPME).

An alternative to conventional solvent extraction methods has been the development of artificial mouths, where the retronasal volatile compounds are evaluated. In this electronic device, artificial saliva acts as an extractant and several motors imitate the mastication. Once the volatiles are trapped in the artificial mouth, they are analysed by SPME-GC [17]. Artificial mouths allow the release of similar volatile compounds as in the human mouth. Gas sensor arrays could be coupled in order to detect aftertaste volatile compounds.

In order to find the volatile compounds that are responsible for the odour quality, olfactometric techniques have also been developed. The AEDA (Aroma Extraction Dilution Assay) method allows the determination of aroma substances by the combination of GC-O (Gas chromatography-olfactometry) with GC/MS or GC/FID [18]. Thus, GC-O/MS gives information about marker substances capable of being detected by a sensory test panel since odourant compounds are addressed at the same time to the MS or FID detector and to the human nose. Olfactometric techniques really establish a connection between sensory and chromatographic analysis.

Therefore, the aim of this review is to collect and interconnect the current alternatives in the analysis of volatile compounds in wheat bread, presenting moreover the advantages and drawbacks.

2. Extraction methodologies employed in wheat bread aroma

To determine bread aroma, firstly it is necessary to extract the volatile compounds from the matrix. The different extraction methodologies are described hereafter, and the main applications summarised in Table 1, where the most relevant volatile compounds studied in the literature are collected [19].

2.1. Solvent extraction methodology

The analysis of bread aroma could only be made with crumb, crust, or with a mix of both. If only the crust or crumb is submitted to analyses, the first step is to separate the crumb and crust carefully from each other. Then, the crumb and/or crust should be frozen with liquid nitrogen in order to attach the volatile compounds and block the biochemical evolution. Finally, the frozen sample should be grounded to a powder with a mortar and a pestle or with a blender [20,21]. If necessary, the powder could be spiked with an internal standard (IS) prior to extraction. Onishi et al. [22] employed 3-heptanol as IS for both crumb and crust analyses. 2-methyl-3-heptanone has been also reported as an IS for crust aroma analysis [21]. Antioxidants, like BHT, have been also utilised in spiked samples in order to prevent oxidation [21].

However, most of the researches that employed IS have carried out Stable Isotope Dilution Assay (SIDA). It is a quantification method that employs isotopically labelled analogues of the analytes as IS, in order to quantify with a high level of precision and accuracy [23]. The most preferred have been deuterium label or carbon-13 label. Thus, Moscowitz et al. [21] quantified methional and 4-hydroxy-2,5-dimehtyl-3(2H)-furanone with their deuterated labelled analogue while 2,4-dihydroxy-2,5-dimehtyl-3(2H)-furanone was quantified with its carbon-13 labelled analogue. However, Zehentbauer and Grosch [24] employed carbon-13 labelled analogue to quantify 4-hydroxy-2,5-dimehtyl-3(2H)-furanone (opposite to Moscowitz et al. [21]), 2,3-butanedione and acetic acid, but deuterated analogue in the seventeen remaining quantified volatile compounds. The choice of