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## REVIEWS

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### Analysis of Volatile Compounds and Their Contribution to Flavor in Cereals

Meixue Zhou,<sup>†</sup> Kevin Robards,<sup>\*,†</sup> Malcolm Glennie-Holmes,<sup>‡</sup> and Stuart Helliwell<sup>†</sup>

School of Science and Technology, Charles Sturt University, P.O. Box 588, Wagga Wagga 2678, Australia,  
and Agricultural Research Institute, NSW Agriculture, Wagga Wagga, Australia

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Recent developments in methods for isolation and measurement of volatiles from cereals are reviewed. The main types of isolation methods, namely, direct extraction, distillation, and headspace, have recently been complemented by solid phase microextraction. Direct solvent extraction provides efficient recovery of compounds with a broad range of polarities and volatilities, whereas headspace techniques provide relatively clean extracts. Supercritical fluid and solid phase microextractions have not yet been fully evaluated for cereals. GC and GC/MS remain the dominant techniques for measurement of the extracted compounds, although new electronic noses show promise. Relating these results to human perception requires careful control to ensure valid comparisons and, in this respect, aroma extract dilution analysis is a useful procedure.

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**Keywords:** *AEDA; aroma; cereal; flavor; analysis*

#### INTRODUCTION

Flavor depends on a multifaceted series of sensory responses including tastes—sweet, sour, salty, bitter, and umami—and olfactory responses, which involve a virtually unlimited number of descriptors, and the additional oral sensory sensations mediating coolness, astringency, and pressure, referred to as chemisthesis mediated through the trigeminal system (Labows and Cagan, 1993). However, as stated by Hornstein (1966) “The factor which has the greatest influence on flavor

is odor. If a food has no odor, its “flavor” is gone and it is experienced primarily in terms of bitter, sweet, sour, and salt”.

Many factors complicate the task of analysis of aroma. The compounds that contribute to the aroma of a food are usually present in trace to ultratrace amounts comprising a diverse range of classes of chemical compounds. This chemical diversity may be further enhanced by subsequent processing. The physical properties of these compounds are equally diverse, extending from that of the permanent gases to substances with boiling points exceeding several hundred degrees. This facilitates separations but complicates simultaneous recovery of the full range of aroma compounds. Methods used to assess the aroma compounds contributing to flavor in cereals are reviewed. Despite their differences (Zhou et al., 1998), cereals have a common feature in

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\* Author to whom correspondence should be addressed (telephone 02 6933 2547; fax 02 6933 2737; e-mail krobards@csu.edu.au).

<sup>†</sup> Charles Sturt University.

<sup>‡</sup> NSW Agriculture.

that they are characterized by very low levels of aroma compounds, particularly in the unprocessed grains. Flavor-related studies on bread (wheat), rice, and corn far exceed those on other cereals. The correlation of volatiles with cereal flavor, which is also examined, is complicated by a number of factors. For instance, different aroma profiles exist at different times during mastication of food due to the effects of hydration (Clawson et al., 1996).

#### ANALYTICAL METHODS

The emphasis in flavor studies has been the identification of volatiles in foods, the mode of formation of these volatiles, and their correlation with sensory data. Quantitative measurements have received much less attention, although the same chemicals can contribute to flavors (Heydanek and McGorin, 1981a) or off-flavors (Heydanek and McGorin, 1981b) depending on their concentration. Detection and identification of volatile compounds are essential, but the correlation of these data with sensory properties is equally important and this requires quantitative data. This is complicated by the inherent differences in the response of the olfactory system and instrumental detectors. The latter are designed for maximum linear detector response, whereas the human olfactory system is nonlinear. Moreover, the extreme sensitivity of the human nose to certain compounds is well illustrated by the work of Chang et al. (1995). Thus, correlation of instrumental and sensory data and identification of what compounds contribute to flavor are complex problems.

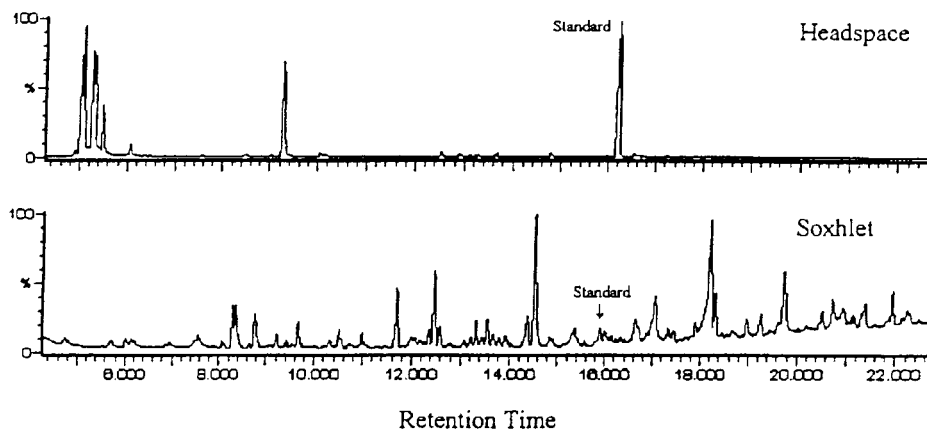
**Sampling.** The classical approach to flavor analysis involves isolation of the aroma volatiles from the food, followed by preconcentration, separation, and identification (Marsili, 1997). The alternative employs model systems to investigate the volatiles formed when appropriate precursors are allowed to react. The latter approach has a number of attractive features including simplicity (the number of components is much smaller) and insight into the reactions that produce aroma compounds. Nevertheless, the classical method is still the favored approach, and the low levels of aroma compounds and limited specificity of analytical techniques mandate the preliminary separation of the flavor compounds. Suitable methods have included many variants of distillation, extraction, and headspace analysis.

The different sampling techniques offer a number of individual advantages but also suffer from specific limitations. Problems common to all techniques are the potential destruction of aroma components and/or production of flavor artifacts. The fidelity between the aroma of the starting material and that of the isolated extract provides the basis for judging analytical techniques. Hence, the conditions employed should be as mild as possible to avoid oxidation, thermal degradation, and other chemical and biochemical changes in the sample. This is particularly important with highly reactive compounds, for example, 2-acetyl-1-pyrroline (Buttery et al., 1997a). However, allowance should be made for the manner in which the food is prepared for consumption. This will determine to some extent the amount to which contact by water and heat might be detrimental. For instance, preparation of rolled oats (typically consumed as porridge at 40 °C) for analysis will normally require procedures different from that used for a muesli bar containing the same oats. Buttery

et al. (1997b) examined both a dry method and a wet method for the isolation of volatiles from popcorn. Most cereals contain minimal quantities of sugars but, even so, the action of heat on sugars during sample processing can produce artifactual flavors. Under these circumstances it may be necessary to pre-extract the aroma component from the cereal prior to any heat treatment. The difficulty arises in distinguishing between artifactual components and those genuinely contributing to flavor. The presence of small but detectable amounts of 2-methyl-, 2,5-dimethyl- and C<sub>4</sub>-substituted pyrazines in commercial oat groats, for example, suggests that some browning occurs during the initial drying process (Heydanek and McGorin, 1986). The qualitative and quantitative aroma profile (Springett, 1990) obtained by solvent codistillation of an aqueous model food system depended on trapping time. Care is therefore necessary in correlation studies using statistical techniques that the conclusions are based on true product aroma and not merely artifacts produced by differences in methodology.

Simple solvent extraction followed by concentration under nitrogen or in a rotary evaporator was one of the earliest methods used to recover "flavor" compounds from foods. Mulders et al. (1973) reported 30 compounds in pentane-ethoxyethane extracts of bread crusts, whereas Richard-Molard et al. (1979) found nearly 100 compounds in French bread when dichloromethane was used as the extracting solvent. However, the low levels of these compounds in cereals plus the level of co-extracted matrix components have generally restricted the application of direct extraction to cereals. Nevertheless, it remains useful for some samples (e.g., bread) (Schieberle and Grosch, 1985) and certain components in other samples that have an indirect role in cereal flavor. Hence, phenolic compounds were extracted from oat flours with aqueous ethanol (Dimberg et al., 1993, 1996) using an Ultra-Turrax homogenizer at room temperature. The extracts were filtered and concentrated by evaporation. On the other hand, sequential or simultaneous distillation/extraction has been widely applied to cereals. Aroma components have been isolated from wheat gluten (Okada, 1969) by steam distillation and extraction with ethoxyethane, from wheat germ (El-Saharty et al., 1997), bread (Folkes and Gramshaw, 1981), extruded triticale (Pfannhauser, 1990), and milled aromatic and scented rices (Tanchotikul and Hsieh, 1991; Laksanalamai and Ilangantileke, 1993; Petrov et al., 1996).

High-vacuum low-temperature distillation or sublimation (Rychlik and Grosch, 1996) generally has advantages for recovery of a broad spectrum of volatiles as shown by Rychlik and Grosch (1996). Toasted bread was extracted with dichloromethane, and the volatiles were isolated by vacuum sublimation and fractionated into neutral/basic and acidic components. In other situations, for example, the recovery of volatiles from cooked rice by steam distillation/solvent extraction (procedure i) gave higher yields and was more rapid than vacuum distillation/solvent extraction (procedure ii) (Tai et al., 1996). The concentrations of volatiles isolated by procedures i and ii and from steam generated during cooking were approximately 0.11–0.42, 0.01–0.10, and 0.05–0.14 mg kg<sup>-1</sup> of cooked rice, respectively. A total of 69 volatile compounds were identified in the extracts obtained by distillation/extraction of cooked rice samples. In other instances, aroma compounds have



**Figure 1.** Chromatograms obtained by GC/MS of a model breakfast cereal comparing headspace and solvent (Soxhlet) extraction. Reprinted with permission from Ropkins and Taylor (1996). Copyright 1996 Royal Society of Chemistry.

been isolated by steam injection/solvent extraction of the cooking water from scented and nonscented rices (Petrov et al., 1996). In general, the use of relatively large samples for volatile recovery has been mandated by the low level of aroma compounds in cereals. Nevertheless, a rapid microscale steam distillation/solvent extraction procedure was used to extract nanogram per gram levels of a "popcorn"-like aroma compound, 2-acetyl-1-pyrroline, from milled aromatic rice (Tanchotikul and Hsieh, 1991). The small sample requirement of 1 g was made possible by improvements in gas chromatographic (GC) separation and mass spectrometric (MS) sensitivity and specificity in the selected ion monitoring mode.

The usual approach in sequential distillation/extraction procedures has involved an initial distillation to isolate volatile components followed by extraction. In contrast, El-Saharty et al. (1997) recovered the neutral constituents of wheat germ by Soxhlet extraction and then isolated the volatile fraction from the lipid matrix by high-vacuum thin-film distillation. The extract was further fractionated by silica gel column chromatography, and the aroma concentrates obtained were analyzed by GC. Simultaneous distillation/extraction remains popular in the aroma research area, and the Likens-Nickerson apparatus has been a standard for a long time (Likens and Nickerson, 1964; Schultz et al., 1977). For instance, aroma compounds were recovered from corn germ protein flour by using the Likens-Nickerson distillation method (Huang and Zayas, 1996). The apparatus is operated at reduced pressure to reduce the sample boiling point and minimize the opportunity for formation of thermally induced artifacts. There are practical difficulties associated with its use, and the low pressure at the solvent side of the apparatus makes it difficult to retain the solvent in the apparatus. Modifications of the apparatus to include a dry ice/acetone condenser followed by a liquid nitrogen trap do not completely eliminate this difficulty. There remains a general concern that simultaneous steam distillation extraction introduces thermal degradation artifacts in cereal aroma analysis (Schieberle, 1995).

One of the most popular methods for flavor isolation has been headspace sampling. Fewer compounds are generally found in headspace extracts than when solvent extraction or distillation methods are used for isolation (Chang et al., 1995). The original headspace procedure involved static recovery [e.g., Molteberg et al. (1996a)] in which the sample was equilibrated in a sealed container and the headspace sample was withdrawn via a septum. Static headspace has been used to

recover volatiles from extruded flaked oatmeal (Guth and Grosch, 1994) and lipid oxidation products from oat groats (Molteberg et al., 1996a). The dynamic procedure (termed purge and trap) involved passing an inert gas through the sample and collecting the stripped volatile constituents in a trap (Chang et al., 1977; Buttery and Ling, 1998). The details differ in the type of trap and loading and unloading of the trap. A cold trap (Badings and de Jong, 1984) has the disadvantage that water is collected with the volatile material. Sorbent traps using charcoal (Sugisawa et al., 1984) or porous polymers (Sugawara et al., 1992; Karahadian and Johnson, 1993; Chang et al., 1995) are common. Buttery and Ling (1995) employed a high-flow dynamic headspace system for recovery of volatiles from corn products, which was improved by incorporation of a closed-loop stripping arrangement in which the sweep gas was recirculated. Distillation has replaced the stripping gas in the initial step (Sugisawa et al., 1984). In this case, volatiles were removed by steam distillation and collected on charcoal, which was dried by passage of clean nitrogen gas. Recovery of the sorbed volatiles from the trap can be achieved by solvent extraction (Sugisawa et al., 1984; Sugawara et al., 1992; Karahadian and Johnson, 1993), microwave (Rektorik, 1983), or thermal desorption (Chang et al., 1995).

The analysis of very volatile compounds by headspace analysis can result in loss of analyte. Dimethyl sulfide (DMS) contributes to the aroma of many foods and has been studied extensively in corn products using methods almost universally based on headspace sampling. However, the extreme volatility of DMS renders the results of these studies suspect (Breedon and Juvik, 1992). Potential losses have been avoided by using toluene extraction and exploiting the high solubility of DMS in toluene.

Headspace analysis, conventional solvent extraction and supercritical fluid extraction (SFE) have been compared for the sampling of a model breakfast cereal (Ropkins and Taylor, 1996). Headspace produced a clean extract (Figure 1) but was inherently unsuited to sampling of higher-boiling nonvolatile components and tightly bound and encapsulated volatiles. These substances required the more aggressive sampling of Soxhlet extraction (Figure 1). There are, however, many disadvantages associated with solvent extraction including contamination of the flavor components with unwanted material such as lipids and nonaroma hydrocarbons. The two profiles of Figure 1 appear to be very different, but many of the compounds were common



**Table 1. Comparison of Recovery of Volatiles from a Model Breakfast Cereal Using Soxhlet and Supercritical Fluid Extraction (Ropkins and Taylor, 1996)**

compound	Soxhlet extraction		SFE extraction		rel recov (%)
	concn (ng g <sup>-1</sup> )	RSD (%)	concn (ng g <sup>-1</sup> )	RSD (%)	
3-methylbutanal	92	22	128	17	140
dimethyl disulfide	60	20	0	0	0
hexanal	412	8	378	12	92
2-methylpyrazine	14	12	10	17	70
2-furancarboxaldehyde	232	10	241	19	104
2-furan methanol	1128	11	1479	18	131
C <sub>2</sub> -pyrazine	22	13	14	20	64

to both methods of recovery. Variation in the relative amounts of these compounds was attributed to differences in volatility and sample-headspace partitioning, which affected the headspace more significantly than the Soxhlet extract. Solvents used for solvent extraction and desorption must be of the highest purity to avoid background noise following concentration of extracts.

Supercritical fluids have often been incorrectly equated with super solvents. This is not the case, and the real advantage of such materials is the ability to fine-tune the solvating power by optimizing extraction temperature and pressure and, by the addition of organic modifiers, to selectively fractionate a sample (King, 1998a,b; Valcarcel and Tena, 1997; Burford et al., 1997). In dynamic SFE, the flow rate can also be optimized. Using a model breakfast cereal, recovery of volatile substances by SFE (Table 1) was comparable with that achieved by conventional extraction using a Soxhlet apparatus (Ropkins and Taylor, 1996). SFE reduced coextracted material, primarily lipids and extended chromatographic column lifetimes.

Solid phase extraction techniques have been applied both in the isolation and in the cleanup of flavor extracts (Penton, 1997; Coulibaly and Jeon, 1996). In a typical application, aroma components recovered by solvent extraction (Uhlig et al., 1987) or distillation (Heymann et al., 1986) were passed through a suitable cartridge. The range of phases available in such cartridges is now comprehensive, and a suitable sorbent can be chosen to retain the aroma compounds while allowing elution of interfering materials or vice versa. The former approach is used most commonly because it permits simultaneous concentration of the extract. Recently, solid phase microextraction (SPME) has been widely used to detect volatile and nonvolatile compounds at the trace and ultratrace levels (Boyd-Boland, 1998; Bartelt, 1997). The technique utilizes a short length (e.g., 1 cm) of fused silica coated with an adsorbent. The coated fused silica (SPME fiber) is immersed directly into an aqueous sample or into the headspace above a liquid or solid sample. For reproducible results a number of variables must be controlled during the sorption process. These include polarity and thickness of the coating on the fiber, sample agitation, the sampling method (headspace versus immersion), sample pH, salt content, and volume (Pawliszyn, 1997). The control of sampling time and temperature and, in the case of immersion sampling, the depth of fiber immersion is critical. Following sorption, the fiber is transferred directly to the injection port of a GC where thermal desorption takes place.

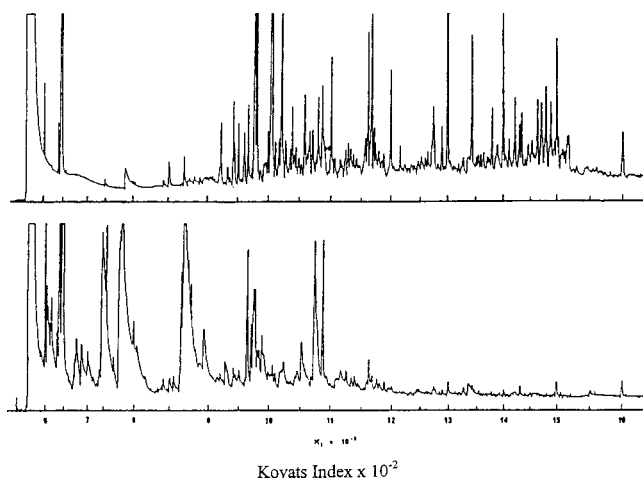
The advantages of SPME include solvent-free and rapid sampling, low cost, ease of operation, and sensitivity (Pawliszyn, 1997). The technique has had limited application to cereals (Zhou et al., 1999). Aroma com-

pounds released during microwave heating of spaghetti have been collected (Roberts and Pollien, 1997) in a system employing a series of cold traps. Compounds from the various traps were quantified following SPME. Studies have been conducted on standard compounds (Bartelt, 1997; Yang and Peppard, 1994) and model solutions (Ibañez and Bernhard, 1996), but detailed studies are required to compare different fibers [e.g., poly(dimethylsiloxane) and polyacrylate] and to investigate optimum extraction conditions for cereals [cf. Elmore et al. (1997)]. For the recovery of pyrazines from model solutions, headspace SPME gave results comparable to those with conventional solvent extraction with dichloromethane (Ibañez and Bernhard, 1996). Pyrazines are important constituents of cereal flavor. Maillard reaction products, which are also important to flavor, have been determined (Coleman, 1997) using SPME on polar and nonpolar fibers. Both fibers demonstrated a tendency to selectively adsorb the more highly alkyl-substituted compounds relative to their comparable proton-substituted analogues. The more polar fiber exhibited greater selectivity for the more polar Maillard reaction products. The amount of adsorbed material was greatly enhanced by the addition of sodium chloride to the aqueous samples. The artifactual formation of aroma compounds as Maillard reaction products in the injection port of the GC has been noted (Verhoeven et al., 1997), and suitable precautions such as prewashing of the fiber should be adopted.

The loss of more polar materials by adsorption is a potential problem in methods using solid sorbents. On the other hand, countercurrent chromatography (Conway, 1990) in its many variants has the advantage that it does not employ a solid sorbent, thus allowing recovery of polar and readily absorbed compounds such as labile flavor precursors under gentle conditions. Volumes of solvent are much less than in solvent extraction. Nevertheless, countercurrent chromatography has not been applied to cereals.

**Measurement.** The classical methods used to determine the aroma constituents were physicochemical techniques and sensory analysis (not discussed here). Aroma is multivariate, and physicochemical techniques for its measurement have been dominated by the separation sciences, particularly high-resolution GC and high-performance liquid chromatography (HPLC) with various coupled techniques.

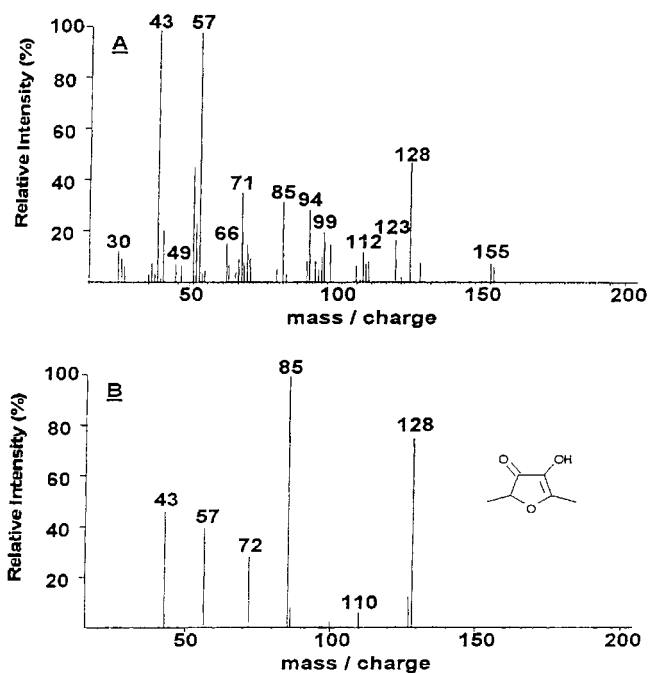
Phenolic acids may contribute to flavor either directly or indirectly by influencing the rate of lipid oxidation by acting as antioxidants. From a comparison of detected levels and reported flavor thresholds, phenolic acids are expected to contribute significantly to objectionable flavors in wheat but not in oats (Sosulski et al., 1982; Maga and Lorentz, 1973). However, the flavor threshold is lowered by synergism (Maga and Lorentz, 1973), and phenolics may still contribute indirectly to oat flavor. HPLC is widely used for the determination of phenolic acids in cereals (Molteberg et al., 1996b). For example, ferulic acid (4-hydroxy-3-methoxycinnamic acid), the major phenolic acid in wheat, has been determined by HPLC with ultraviolet or fluorescence detection (Wetzel et al., 1988) using a method optimized for selective detection of cinnamic acids. The use of HPLC has been much less common for the determination of volatile aroma compounds traditionally associated with flavor. In the latter application area, GC has



**Figure 2.** Chromatograms of total volatiles isolated from dry oat groats (top) and hydrated oat groats (bottom) on an SE30 capillary column with flame ionization detection. Detector response:  $\times 256$  and  $\times 1$ , respectively. Reprinted with permission from Heydanek and McGorin (1981a). Copyright 1981 American Chemical Society.

dominated (Huang and Zayas, 1996; Buttery and Ling, 1995; Nitz et al., 1989), typically using high-resolution columns (30 m or longer) with relatively nonpolar phases (Heydanek and McGorin, 1981a,b), although more polar phases may assist with difficult separations (Buttery et al., 1997a,b). For headspace analysis with thermal desorption, cryofocusing at the top of the GC column is often necessary to produce narrow sample inlet bands (Chang et al., 1995).

In a typical application, volatiles recovered from extruded triticale by distillation/extraction were analyzed by GC/MS and GC/olfactometry (Pfannhauser, 1993, 1990). Twenty-three aroma volatiles detected in fresh samples were classified into two groups as compounds originating from the lipids of the germ by oxidation processes (e.g., hexenal, hexanol) and pyrazines formed as Maillard products by reactions of proteins and starch. Some of these compounds have also been identified in the aroma of fresh bread. A similar approach involving microscale steam distillation/solvent extraction and GC/MS was used (Tanchotikul and Hsieh, 1991) to determine 2-acetyl-1-pyrroline, a popcorn-like aroma compound in milled aromatic rice. Complex aroma profiles have been resolved by GC as demonstrated by the chromatograms of Figure 2, which also illustrate the effects of both sample preparation and isolation procedure on the chromatogram. However, even with the best columns, resolution is still probably insufficient to resolve all components of a complex mixture. In such cases, interpretation of the data is complicated by contaminated peaks, and multidimensional chromatography or coupled techniques including GC/MS (Shen and Hoseney, 1995) have proved invaluable. For instance, multidimensional GC (Nitz et al., 1989) has been used to determine 2-methylisoborneol and geosmin as the compounds responsible for a "musty-earthly" off-odor in wheat grains. The benefit of tandem MS is illustrated in Figure 3, which shows a contaminated mass spectrum (Fay et al., 1996) of 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, which did not allow unambiguous identification of this Maillard product. On the other hand, the daughter mass spectrum of the same compound (Figure 3) is free of interference and provided definitive identification.



**Figure 3.** Electron impact ionization mass spectra of 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone formed in a Maillard reaction system comprising pentose and glycine. Spectrum A was obtained by EI at 70 eV of the chromatographic peak, and spectrum B is the product ions after collision-induced dissociation (10 eV) of the molecular ion at  $m/z$  128. Reprinted with permission from Fay et al. (1996). Copyright 1996 Royal Society of Chemistry.

A number of coupled techniques combine the advantages of the high resolving power of chromatography with the capacity of spectrometry for compound identification. The various techniques are complementary as seen in the development of GC/MS and GC/Fourier transform infrared spectrometry (GC/FTIR). GC/MS is ideally suited to identification and structural elucidation of compound homologues but less suited to identification of isomeric species, a situation reversed with GC/FTIR. This is illustrated (Chang et al., 1995) by the identification of 74 volatile compounds including 18 alcohols, 15 aldehydes, 5 ketones, 5 esters, 1 lactone, 1 hydroxy-ketone, 13 pyrazines, 2 pyrroles, 4 hydrocarbons, 2 sulfur compounds, and 8 other compounds in bread crust using GC/FTIR/MS. Additional confirmation of structures was provided by retention indices. Mass spectral data and retention indices (and odor quality) of the eluting peaks have been used in many other studies [e.g., Karahadian and Johnson (1993)] to assist in assigning structure. However, identification of the eluted species (as distinct from correlation with aroma) is usually incomplete, and presentation of the retention data as retention indices (e.g., Kovats) is a useful method in such instances (Heydanek and McGorin, 1981a,b).

Chromatograms may be complicated by resolution of tautomeric species as in the case of 2-acetyltetrahydropyridine (Schieberle, 1995), which is separated by GC on a specially deactivated stationary phase into two tautomers that showed identical electron impact and chemical ionization mass spectra. On the other hand, separation of stereoisomers is difficult, and yet enantiomers can contribute significantly different flavor sensations. The importance of enantiomeric separations to aroma has been recognized, although this aspect has been neglected in cereal analysis. The traditional ap-

proach to separating chiral compounds exploited chiral derivatization agents with achiral stationary phases (Stalcup et al., 1993). Alternatively, the development of chiral stationary phases based on modified cyclodextrins has provided excellent GC separations of many enantiomeric compounds (Betts, 1994).

Quantification of the eluted species is relatively straightforward (providing adequate sampling procedures have been adopted) in determinations involving a single analyte (Tanchotikul and Hsieh, 1991) but is complicated in more usual cases by the large number and chemical diversity of volatile compounds. Selection of appropriate internal standard(s) is then difficult, although toluene has been used (Molteberg et al., 1996a) in this capacity to quantify a broad range of volatiles. This also highlights the difficulties associated with obtaining reference standards, which are often not available commercially and chemical synthesis is time-consuming and expensive. For example, 150 chemicals and 37 key odorants were identified (El-Saharty et al., 1997) by GC/MS and GC/olfactometry in wheat germ extracts obtained by Soxhlet extraction and high-vacuum thin-film distillation. Similarly, GC/MS identified in excess of 92 compounds in aroma extracts of rice miso (Sugawara et al., 1992), 69 volatiles in cooked rice (Tai et al., 1996), and several pyrazines in corn products (Karahadian and Johnson, 1993).

Stable isotope dilution analysis is also a powerful technique that has allowed accurate quantification of several compounds in popcorn (Schieberle, 1995) and toasted bread (Zehentbauer and Grosch, 1997, 1998a,b). In this procedure, isotopomers are used as internal standards, and many of these must be synthesized (Zehentbauer and Grosch, 1998a). The procedure provides highly accurate measurements because unavoidable losses of analyte during isolation are ideally compensated, although the timing of addition of the spike must be considered. Zehentbauer and Grosch (1998a) quantified several volatiles in white bread crusts using stable isotope dilution analysis. The bread crust was frozen in liquid nitrogen and then ground before being spiked with the relevant isotopomers. The chemical state of the spike vis-à-vis the native analytes is a potential concern as is adequate mixing of the spike and sample. These are relatively minor considerations, and stable isotope dilution analysis represents state of the art in quantification (Debievre and Peiser, 1997; Catterick et al., 1999).

Chromatographic measurements require resolution of the aroma constituents, and the aroma sensation is then reconstructed using various statistical approaches. An alternative approach involves electronic noses comprising arrays of gas sensors with an associated pattern recognition technique (Talou et al., 1996). These devices do not measure any volatile compound singly, and the signals obtained are correlated with "bulk volatiles". Electronic noses have been applied to aromatic rices (Moon et al., 1996) and the classification of grain samples based on their smell and the prediction of the degree of moldy/musty odor (Börjesson et al., 1996). Headspace samples from heated grains were pumped through chambers containing metal oxide semiconductor field effect transistor sensors, SnO<sub>2</sub> semiconductors, and an infrared detector monitoring CO<sub>2</sub>. Sensor signals were evaluated with a pattern recognition software program based on artificial neural networks. Nevertheless, electronic noses have had limited application to

cereals, and it seems unlikely that the sensors agree in sensitivity and specificity with the human perception of odorants.

#### RELATING INSTRUMENTAL RESULTS TO HUMAN PERCEPTION

A pair of 1964 papers (Hrdlicka and Janicek, 1964a,b) describing the presence of carbonyls, bases, and an alcohol in toasted oat flakes were the first reports of the volatile component of oats. The authors regarded carbonyls as one of the factors relating to the nutlike flavor of toasted oat flakes but stated that these compounds were not totally responsible for the flavor perceptions. Heydanek and McGorin [as quoted in Heydanek and McGorin (1981a)] reported at a conference in 1980 that pyrazines were also important to the overall perception of oat flavor. A similar historical pattern emerges with other cereals in which the emphasis in early studies was placed on the isolation and identification of volatile components. A multiplicity of compounds were identified particularly when solvent extraction was used. These compounds were associated with the flavor of cereals [see Teranishi (1989)], and many were found to be common to wheat, rice, barley, oats, and corn (Legendre et al., 1978; Okada, 1969; Hrdlicka and Janicek, 1964b; Bullard and Holguin, 1977). However, the identified compounds did not appear to provide all of the flavor sensations associated with these grain sources (Heydanek and McGorin, 1986). The development and refinement of headspace techniques provided a system that measured volatile and presumably aroma-related compounds without the interference of nonvolatiles. Such developments witnessed a further rapid increase in the number of compounds identified in cereals and associated with flavor. This flood of information led to the concept of key components. Recent studies also suggest that the number of volatiles significant in determining flavor (Grosch, 1994) may be less than previously supposed.

Efforts were made to correlate the special flavors of cereals to specific volatile compounds or groups of compounds. Yajima et al. (1978) felt that the oxygenated neutral fraction was the major contributor to cooked rice flavor and that these volatiles originated during the cooking process by lipid oxidation. Withycombe et al. (1978) attributed the toasted flavor notes and the tealike aroma of wild rice to the pyrazine and alkylpyridine components, respectively. 2-Acetyl-1-pyrroline was first found to be important to the flavor of aromatic rices (Buttery et al., 1983) and later to the aroma of bread crust (Schieberle and Grosch, 1985) and popcorn (Schieberle, 1991). Yajima et al. (1983) described 209 compounds isolated from boiled buckwheat flour. The basic fraction had a nutty and slightly fishlike odor. The pleasant nutty aroma was attributed to several pyrazines with the fishlike odor being due to pyridines. Both groups of compounds were thought to have been formed by the Maillard reaction. Extensive fractionation of the neutral components isolated a fraction comprising mainly alkanals (green odor), whereas another fraction contained a characteristic aroma of boiled buckwheat flour but contained 55 compounds. The authors concluded that boiled buckwheat flour aroma was very complex and was composed of the combined aroma effects of many components.

Flavor is inherently multivariate; it represents a composite response that cannot be duplicated by sum-



mation of responses to individual peaks in a chromatogram. The vast number of substances separated in a typical analysis that may or may not have some relationship to aroma mandates the use of sophisticated statistical procedures (Huang and Zayas, 1996) to determine which compounds in which particular combination have significant effects on flavor perception. Statistical correlations of instrumental and sensory measurements based on linear regression are limited, whereas multivariate procedures have been more successful in correlating the two sets of data. In one approach multivariate statistics are used to determine which chromatographic components are most highly correlated with the sensory data. This approach accurately models the synergistic nature of aroma-active and nonactive components. For instance, significant positive correlations between preference for total flavor and amounts of isobutylaldehyde, propionaldehyde, 2-butanone, and some unidentified compounds in French bread were found (Hironaka, 1986), whereas significant negative correlations were found between this preference and levels of ethanol and isobutanol. Fourteen GC/MS peaks selected by stepwise discriminant analysis (Sugawara et al., 1992) accounted for 76% of variation in aroma scores between rice miso samples. Using these 14 peaks and canonical discriminant analysis, all rice miso samples were classified into their correct sensory score group. Univariate and multivariate statistical procedures were used (de Leon, 1994) to treat sensory data, collected from ready-to-eat breakfast cereals using quantitative descriptive analysis (QDA). By this approach, 13 of 16 sensory descriptors generated by trained panelists were shown to be discriminators, and these were reduced by factor analysis into 3 orthogonal factors with minimal loss of information.

The disadvantage is that some compounds may be selected for the flavor model because they were highly correlated but not causative agents, and any change in the sample set will then produce a new set of components requiring a new model. Peaks that do not produce a detector response are also neglected in such correlations. These limitations can be minimized by using data from GC/olfactometry (El-Saharty et al., 1997; Huang and Zayas, 1996; Pfannhauser, 1993, 1990), which has been extended to a time-intensity approach for evaluating the aroma significance of compounds in the GC effluent (da Silva, 1994).

The first formal approach to establish which volatiles contributed to odor was the calculation of the ratio of concentration of the volatile compounds to their odor thresholds. Results were referred to as aroma values, odor units (Guadagni et al., 1966), or odor activity values (OAV) (Acree et al., 1984). The so-called character-impact odorants were distinguished from other volatiles with low or no odor activity by calculation of OAV. Charm analysis (Acree et al., 1984) or aroma extract dilution analysis (AEDA) (Ullrich and Grosch, 1987) has revolutionized the process of odorant identification. In both procedures, an extract of the food is assessed by GC/olfactometry; the extract is then diluted, usually as a series of dilutions, and each dilution is reanalyzed. The result is expressed as a flavor dilution (FD) factor, which expresses the ratio of the concentration of the odorant in the initial extract to its concentration in the most dilute extract in which an odor was detected.

The application of AEDA to bread, rice, and corn products has been reviewed by Grosch and Schieberle

(1997), and only the salient features are presented. Studies on the volatile components of unprocessed wheat are few in number. Bread flavor has attracted considerably more attention, but the complex fermentation processes involved preclude extrapolation to the whole grain or flour. The key odorant evoking the roasty note in the aroma profile of wheat bread crust has been confirmed as the popcorn-like-smelling 2-acetyl-1-pyrroline (Grosch and Schieberle, 1997; Schieberle and Grosch, 1991). This compound was very low in rye bread, which was much higher in 3-methylbutanal and methional. The results of AEDA further suggest that various furanones and acetic acid are higher in rye bread crust. The differences in the overall odors of wheat and rye bread were attributed to the variations in these key odorants. On the other hand, the most potent odorants of wheat bread crumb based on high FD factors were 2-phenylethanol, (*E*)-2-nonenal, and (*E,E*)-2,4-decadienal. The key odorants in toasted wheat bread crumb have also been assigned (Rychlik and Grosch, 1996) by AEDA. In one of the few studies on wheat germ, volatile, neutral constituents obtained by Soxhlet extraction (El-Saharty et al., 1997) were analyzed by GC, coupled GC/MS, and GC/olfactometry. Application of AEDA revealed 37 key odorants among the 150 compounds in the original concentrate. Seven of the 37 important aroma compounds of wheat germ showed very high FD factors (range =  $2^7$ – $2^9$ ): *n*-hexanal (grassy-flowery), *n*-octanal (fatty), *n*-nonanal (floral, fatty), (*E*)-2-octenol (green, herbaceous), (*E,E*)-2,4-nonadienal (oily), (*E,E*)-2,4-decadienal (fatty), and 4-octanolide (coconut, creamy).

There is a distinction in the key odorants between fragrant and nonfragrant rices (Grosch and Schieberle, 1997). Aroma compounds were isolated (Petrov et al., 1996) by steam injection/solvent extraction of the cooking water from a scented rice and a nonscented rice and analyzed by GC. Seventy-eight compounds were identified in the extracts, and the major difference between cultivars was in the concentration of 2-acetyl-1-pyrroline, which was a major constituent of the volatiles from the scented variety but was not detected in the volatiles from the nonscented variety. As noted, this compound is a significant contributor to the aroma of several cereal products (Grosch and Schieberle, 1997; Tanchotikul and Hsieh, 1991).

The aroma of corn and corn products (tortillas, popcorn) has been extensively studied. The concentrations of volatiles in canned corn products were generally many times higher than those in frozen and fresh products (Buttery et al., 1994). Major volatiles common to all three products included dimethyl sulfide, 1-hydroxy-2-propanone, 2-hydroxy-3-butanone, and 2,3-butanediol. Pyridine, pyrazine, alkylpyrazines, and 2-acetylthiazole were additional major components in canned products but minor components in fresh and frozen products. Comparisons of calculated odor units indicated that the compounds most important to canned sweet corn aroma included dimethyl sulfide, 2-acetyl-1-pyrroline, 2-ethyl-3,6-dimethylpyrazine, acetaldehyde, 3-methylbutanal, 4-vinylguaiaicol, and 2-acetylthiazole. Alkylpyrazine and 3-methylbutanal were less important to fresh sweet corn aroma, whereas 2-acetyl-2-thiazoline was important. The compound 2-aminoacetophenone was identified as a prominent volatile in tortillas and taco shells (Anonymous, 1994). The odor quality of this ketone was characterized by GC/olfactometry as the

typical flavor impression of tortillas. It showed the highest OAV in tortillas and was among the highest in taco shells (Buttery and Ling, 1995; Karahadian and Johnson, 1993). Several other compounds were identified as important to the overall flavor. Application of AEDA (Schieberle, 1991) to freshly prepared popcorn revealed 23 odorants, among which 2-acetyl-1-pyrroline (roasty, popcorn-like), (*E,E*)-2,4-decadienal (fatty), 2-furfurylthiol (coffee-like), and 4-vinyl-2-methoxyphenol (spicy) predominated with the highest FD factors. Further potent flavor compounds showing roasty odors were 2-acetyltetrahydropyridine and 2-propionyl-1-pyrroline. More recently, data have been reported (Buttery et al., 1997b) for microwave oven-produced popcorn. The results confirmed previous studies, and some additional compounds were identified in popcorn for the first time. The latter included dimethyl sulfide, dimethyl di- and trisulfides, 3-methylindole (skatole),  $\alpha$ - and  $\beta$ -ionones, 2-methyl-3-hydroxypyran-4-one (maltol), 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, 5-methyl-4-hydroxy-3(2*H*)-furanone (norfuranol), geranyl acetone, and others. Hydrogen sulfide was found as a major component of the volatiles emitted during popping. The method of preparation impacted significantly the aroma profile (Grosch and Schieberle, 1997).

The flavor components in oats are similar to those in other cereals, but oats present a somewhat unique and characteristic flavor in the cereal grain family. Their nutty, pleasant grain character is obviously highly acceptable to a great number of consumers (Heydanek and McGorin, 1986). In their pioneering studies, Hrdlicka and Janicek (1964a,b) reported on the nutlike flavor of toasted oat flakes. GC/MS studies have identified >100 compounds in the total volatiles fraction of oats, 35 compounds in headspace volatiles of oat groats (Heydanek and McGorin, 1981a), 45 volatiles obtained from vacuum steam distillation of rancid oat groats (Heydanek and McGorin, 1981b), and nearly 100 compounds in toasted oat groats (Heydanek and McGorin, 1986). However, oats lack flavor as collected from the field, and the aroma/flavor that is associated with oat products requires the intervention of a heat process to develop (Heydanek and McGorin, 1986; Fors and Schlich, 1989). Nevertheless, steam treatment alone is not effective for flavor development in oats, which requires direct heat in the kiln without which oat products retain a flat, green taste, that is, raw and slightly bitter (Gansmann and Vorwerck, 1995).

Heydanek and McGorin (1981a) found dramatic differences between the profiles and relative concentrations of volatiles obtained by vacuum steam distillation and dry vacuum isolation from groats. Volatiles were collected in a series of cold traps following vacuum distillation of dried or hydrated groats and then recovered by extraction with dichloromethane. The sample size (8 kg of oats) and concentration factor attest to the low level of volatiles in the oats. The results were compared with those obtained by dynamic headspace analysis using a porous polymer as sorbent. Thermal desorption directly into the injection port of the GC/MS was used with cryogenic focusing of the desorbed volatiles. The headspace procedure was designed to identify lower boiling components, whereas the distillation procedure was intended to evaluate materials with Kovat's indices exceeding 600. The profiles obtained by the different methods showed significant differences. For example, a major peak such as limonene

in the dry vacuum isolate represented a 10 ng g<sup>-1</sup> concentration, whereas hexanal in the hydrated isolation was present at 3–5  $\mu$ g g<sup>-1</sup>. The dry vacuum isolate, which represented the weak grainy, haystraw odor of dry groats, contained mostly hydrocarbon materials with C<sub>10</sub>H<sub>16</sub> terpenes, alkylbenzenes, and some oxygenated constituents as the principal components. Hexanal, with a concentration <50 ng g<sup>-1</sup>, was the major oxygenated compound. The alkylbenzenes were attributed to contamination of the groats in the natural environment and would not be expected to be of importance to the overall flavor of oat groats or their products. The weak hay, grassy odor of dried oat groats derives from very low levels of monoterpenes and hexanal. In contrast, there was a much higher level of oxygenated compounds in the volatiles isolated by vacuum steam distillation together with a completely different profile of components. The distillate had a more green cereal-type odor and flavor. Major components were 3-methyl-1-butanol, 1-pentanol, 1-hexanol, hexanal, 1-octen-3-ol, (*E,E*)- and (*Z,E*)-3,5-octadien-2-one, and nonanal. The dienones probably arose from a chemical or enzymatic lipid oxidation reaction. Many other components associated with enzymatic activity were found, including several alcohols and aldehydes. Traces of the major components from the dry vacuum isolate were also found in the hydrated isolate. The authors suggested that when the isolation was carried out in the presence of water, considerable enzymatic activity was still present in the dried oat groat, and the volatiles produced by this activity were superimposed on the volatiles inherent in the dry groat. The results suggest that the flavor of oat products will depend greatly on the processing method.

A knowledge of the changes in volatiles induced by processing and storage is important and has been studied in oats. The effects of heat treatment and processing on the development of the oaty–nutty flavor of cooked oatmeal have been investigated (Heydanek and McGorin, 1986; Fors and Schlich, 1989). Heydanek and McGorin (1986) used the same basic approach as in their earlier work to examine volatiles at various stages of production except that the oatmeal volatiles were further fractionated into basic and acid/neutral fractions. For the basic fractions of oat groats, uncooked and cooked oatmeal, an increase in the development of the oaty–nutty flavor was accompanied by an increase in the complexity and concentration of nitrogen heterocycles. The higher concentrations of *N*-heterocycles in basic fractions from volatiles isolated by Nickerson–Likens distillations were considered artifacts due to the more severe conditions of isolation. This demonstrates that oatmeal has the potential for further flavor development under appropriate conditions.

The neutral fraction changed dramatically across the stages of oatmeal preparation. As noted, the inherent components of oat groats are present in low concentrations and contribute little to the volatile profile and flavor. However, volatiles appeared after the rolling and flaking operation with its associated heating steps, although the levels were still quite low. Oxygenated components were the most abundant neutrals in cooked oatmeal, for which the flavor volatiles were mostly derived from lipid oxidation processes and from interactions of reducing sugars and amino acids. These compounds included pentanal, furfural, heptanal, benzaldehyde, 1-octen-3-ol, 2,4-heptadien-1-al, phenylacetaldehyde, 3,5-octadien-2-one, 2,4-nonadien-1-al,  $\gamma$ -octalac-



tone, 2,4-decadien-1-al, and  $\gamma$ -nonalactone. There was no single component to which "oaty" flavor might be attributed, but rather the flavor of cooked oatmeal was a blend of the impressions contributed by basic nitrogen heterocyclics and the neutral components. Fors and Schlich (1989) also indicated many heterocyclic species were important flavor compounds in heated food items and that these compounds were normally isolated in the basic fraction.

The potential for further flavor development in oats is exploited in the production of toasted oat flakes or groats (Heydanek and McGorin, 1986). Volatiles were recovered from toasted groats by steam distillation/extraction and separated into basic and acid/neutral fractions. The basic fraction of the isolated volatiles had strong nutty, earthy, toasted, slightly harsh, and burnt flavors, whereas the neutral fraction was described as burnt grain, browned, heavy, and not oaty. The toasted groats contained relatively large amounts, and many more types, of material in the basic fraction than oatmeal. GC/MS of this fraction revealed an extremely complex mixture of various nitrogen heterocycles. The neutral fraction contained >150 components and showed a major shift in the type of components present after toasting compared with the components present in untoasted groats and oatmeal. After toasting, furans (reducing sugar degradation products) become much more abundant. Many of the neutral volatiles in toasted groats can be related to Maillard browning reactions, Amadori rearrangements, and extensive lipid oxidation. The most significant effect on flavor of the application of heat during processing is often associated with the Maillard reaction (Hodge et al., 1972; Mauron, 1981). Recent studies indicate that desirable flavor compounds do not arise exclusively from a classic Maillard system involving reducing sugars and amino acids but rather from interaction between the products of the Maillard reaction and lipid degradation (Huang et al., 1987; Bruechert et al., 1988). For instance, long-chain pyrazines in toasted oats (Heydanek and McGorin, 1986) likely arise from the reaction of dihydropyrazine Maillard intermediates with longer chain alkyl aldehydes from lipid oxidation.

Extruded products present a particular problem because flavor development is limited by the short residence time in the extrusion die and by losses of flavor compounds from the melt leaving the die (Bredie et al., 1998a,b). Volatiles from maize flour extrudates were sampled by purge and trap on Tenax GC (Bredie et al., 1998a) and analyzed by GC/MS after thermal desorption. GC/olfactometry showed that 2-acetyl-1-pyrroline and 2-acetylthiazole contributed important cereal-like odors. Volatiles generated under extrusion conditions of low temperature and high moisture (120 °C, 22%) were associated with products from lipid degradation, the initial stages of the Maillard reaction, and Strecker degradation of amino acids. Extrusion at 150 °C and 18% moisture gave rise to the formation of pyrazines as well as thiophenones possibly derived from reaction of hydroxyfuranones with hydrogen sulfide. Further increase in temperature and reduction in moisture to 180 °C and 14%, respectively, caused a marked increase in the formation of heterocyclics resulting from increased Maillard reaction and cysteine degradation. These conditions were also associated with starch and hemicellulose degradation, as evidenced by the increased level of 2-methoxy-4-vinylphenol. The

level of aldehydes was also decreased, indicating inhibition of lipid degradation by Maillard reaction products. Alternatively, aldehydes may have participated in further reactions with intermediates of the Maillard reaction.

Twenty-five odorants were identified (Guth and Grosch, 1993, 1994) by AEDA in a fresh extrusion product of oatmeal. Of these, hexanal, octanal, *trans*-2,3-epoxyoctanal, (*E,E*)-2,4-nonadienal, (*E,E*)-2,4-decadienal, *trans*-4,5-epoxy-(*E*)-2-decenal, 4-hydroxy-2-nonenic acid lactone, and vanillin appeared with high FD factors. Sjövall et al. (1997) found the major volatiles in stored oat flour extrudate were hexanal, decane, 2-pentylfuran, and nonanal. The relative amounts of these volatiles increased during storage.

#### FLAVOR STABILITY

Two flavor-related issues may arise during cereal storage, namely, reduction in positive flavor notes due to physical processes such as volatilization and/or development of off-flavors. The uptake of diacetyl in extruded starch has been modeled to predict the migration of flavor molecules during storage (Hau et al., 1996), which determines the keeping qualities of some foods. Quantitative information on the migration processes (e.g., diffusion, adsorption) is required to understand the effect of factors such as matrix composition and water content on the migration rates of flavor molecules. The available data were consistent with a composite mechanism for the binding process of diacetyl to starch involving both surface and diffusive mechanisms. Interaction of aroma compounds with other components in a sample is important to flavor intensity (Espinosa-Diaz et al., 1996). In the case of extrusion processing of pregelatinized starches, it seems likely that the starches do not provide appropriate reactive sites and conditions during extrusion for extensive encapsulation of flavor compounds (Kellengode and Hanna, 1997).

Lipid oxidation products and Maillard reaction products were detected among 23 aroma volatiles identified in fresh extrudates of triticale (Pfannhauser, 1990). Aroma compounds were collected by a distillation/extraction procedure, fractionated, and analyzed by GC with peak sniffing. Storage in plastic sacks resulted in considerable losses of aroma volatiles, and after 6 months, only hexanal, 2,4-decadienal, and 5-methylhydroxyacetophenone could be detected. Similar loss of volatiles during storage has been reported for many systems. During short-term 7-day storage of a popcorn sample in a sealed polyethylene bag, the concentration of the roast-smelling popcorn odorants, 2-acetyltetrahydropyridine, 2-acetyl-1-pyrroline, and 2-propionyl-1-pyrroline, decreased by ~70–75% (Schieberle, 1995). The key odorant, 2-acetyl-1-pyrroline, also decreased during storage of fragrant rice (Laksanalamai and Ilangantileke, 1993). In contrast, the concentration of total carbonyls increased during storage of processed and unprocessed rice for 4 months at 37 °C, with the proportions of unsaturated carbonyls, 2-enals, and 2,4-dienals increasing considerably (Semwal et al., 1996). These changes can be attributed to the oxidative degradation of linolenic and linoleic acids.

Rancidity describes the series of autoxidative processes that result in the deterioration in flavor of fatty foods due to the formation of decomposition products. Rancidification is the main limiting factor for the storage and handling of oat products. For instance,

compounds responsible for off-flavor in stored oatmeal extrudate (Guth and Grosch, 1993, 1994) were associated with oxidative deterioration and identified as hexanal, *trans*-2,3-epoxyoctanal, pentanal, and (*E,E*)-2,4-nonadienal. There was no loss of the endogenous antioxidants, ferulic and caffeic acids, during storage, but their distribution altered, declining in the starch lipids and increasing in the nonstarch lipids. Rancid odors in 12-week-old, oat-based, ready-to-eat cereals were correlated (Fritsch and Gale, 1977) with hexanal concentrations of 5–10  $\mu\text{g g}^{-1}$ . Heydanek and McGorin (1981b) investigated the volatile components in noticeably rancid oat groats, which had a pronounced "old oil, rancid, old chicken fat" aroma. They identified 45 compounds including 24 aldehydes, ketones, and alcohols. The most abundant volatiles were hexanal, pentanal, and 3,5-octadien-2-one, which have all been reported in oxidized lipid systems (Forss, 1972). Hexanal was the most abundant volatile, but 2,4-dienals were probably also important (Heydanek and McGorin, 1986) to the perception of the rancid odor as "old chicken fat".

Liukkonen et al. (1992) suggested that prevention of lipid hydrolysis rather than oxidation should be a primary goal in the manufacture of nondeteriorated oat products. The hydrolytic process is initiated by endogenous enzymes, lipases, which are liberated by cell damage. The oat has remarkable lipase activity compared with other cereals (O'Conner et al., 1992), even before germination (Matlashewski et al., 1982; Urquhart et al., 1984; Youngs, 1986), and significant lipolysis can occur even at low moisture levels (Frey and Hammond, 1975) in broken or crushed caryopses. In the production of oat products for human consumption, it is generally considered necessary to inactivate the lipases (Ekstrand et al., 1993) by heat treatment of the groats. Nevertheless, free fatty acid levels increased in stored oats, and the random oxidative breakdown products of the major unsaturated fatty acids can produce the aldehyde and unsaturated aldehyde and ketone volatiles that play a dominant role in the odor and flavor of rancid oat groats (Murray et al., 1976).

Cereal grains also contain a rich variety of phenolic compounds that may contribute to sensory properties (Maga and Lorentz, 1973; Durkee and Thivierge, 1977; Huang and Zayas, 1991). Free phenolic acids are minor compounds in cereals, together rarely exceeding 200 mg  $\text{kg}^{-1}$  of dry weight of whole, mature, undamaged kernels (Collins, 1986). Even at low levels (10–90 mg  $\text{kg}^{-1}$ ), however, free phenolic acids may contribute significantly to objectionable flavors (Maga and Lorentz, 1973; Huang and Zayas, 1991). Dimberg et al. (1996) investigated the phenolic compounds of three oat varieties processed with or without hulls and detected 11 compounds. The levels of vanillic acid, vanillin, and especially *p*-coumaric acid, *p*-hydroxybenzaldehyde, and coniferyl alcohol increased significantly following processing in samples processed with hulls but not in samples processed without hulls. Ferulic acid increased in both samples, whereas caffeic acid and the avenanthramides were found to decrease during processing. The various thermal processes accounted for the main differences in sensory properties of the stored samples (Molteberg et al., 1996b). Twenty-nine percent of the variation in odor and flavor attributes was explained by the 11 phenolic compounds analyzed.

Molteberg et al. (1996a) investigated the storage

stability of raw and heat-treated oat flours (*Avena sativa* L.) by sensory and chemical methods. The stability against lipid oxidation was greatly increased by heat treatment. Volatile compounds were stable in stored raw flours for 5 weeks but increased thereafter, with samples at 42 weeks having an intense paint flavor. There was significant correlation between volatiles and the attributes of paint odor, paint flavor, odor intensity, and flavor intensity, whereas volatiles were negatively correlated to oat odor and flavor. The major volatiles in stored oat flours were hexanal and 2-pentylfuran, and the levels of hexanal and oat flavor were increased in heat-treated oat flours, whereas most volatiles remained constant. The levels of volatiles in heat-treated samples were less well correlated to flavors. Thus, differently heat-treated samples should be assessed separately in future flavor prediction models.

#### LITERATURE CITED

- Acree, T. E.; Barnard, J.; Cunningham, D. G. A procedure for the sensory analysis of gas chromatographic effluents. *Food Chem.* **1984**, *14*, 273–286.
- Anonymous. AACC Committee adopts oat bran definition. *Cereal Foods World* **1989**, *34*, 1033–1034.
- Arberas, I.; Leiton, M. J.; Domínguez, J. B.; Bueno, J. M.; Ariño, A.; de Diego, E.; Renobales, G.; de Renobales, M. The volatile flavour of fresh *Gentiana lutea* L. roots. In *Food Flavors: Generation, Analysis and Process Influence*; Charalambous, G., Ed.; Proceedings of the 8th International Flavor Conference, Cos, Greece, July 6–8, 1994; Elsevier: Amsterdam, The Netherlands, 1995; pp 207–234.
- Badings, H. T.; de Jong, C. Headspace analysis for the study of aroma compounds in milk and dairy products. In *Analysis of Volatiles*; Schrier, P., Ed.; de Gruyter: New York, 1984; pp 401–417.
- Baker, N. R. International trade in oats. In *The Oat Crop*; Welch, R. W., Ed.; Chapman and Hall: London, U.K., 1995; p 62.
- Bartelt, R. J. Calibration of a commercial solid-phase micro-extraction device for measuring headspace concentrations of organic volatiles. *Anal. Chem.* **1997**, *69*, 364–372.
- Betts, T. J. Comparison of two esterified  $\gamma$ -cyclodextrins with some other chirally selective gas chromatographic phases using volatile oil constituents. *J. Chromatogr. A* **1994**, *678*, 370–374.
- Börjesson, T.; Eklöv, T.; Jonsson, A.; Sundgren, H.; Schnürer, J. Electronic nose for odor classification of grains. *Cereal Chem.* **1996**, *73*, 457–461.
- Boyd-Boland, A. Solid-phase microextraction: Solvent-free sample preparation for GC and HPLC. *Chem. Aust.* **1998**, *65*, 10–12.
- Bredie, W. L. P.; Mottram, D. S.; Guy, R. C. E. Aroma volatiles generated during extrusion cooking of maize flour. *J. Agric. Food Chem.* **1998a**, *46*, 1479–1487.
- Bredie, W. L. P.; Mottram, D. S.; Hassell, G. M.; Guy, R. C. E. Sensory characterisation of the aromas generated in extruded maize and wheat flour. *J. Cereal Sci.* **1998b**, *28*, 97–106.
- Breeden, D. C.; Juvik, J. A. An extraction method for the determination of dimethyl sulfide in cooked corn. *J. Food Compos. Anal.* **1992**, *5*, 134–138.
- Bruechert, L. J.; Zhang, Y.; Huang, T. C.; Harman, T. G.; Rosen, R. T.; Ho, C. T. Contribution of Lipids to Volatiles Generation in Extruded Corn-Based Model Systems. *J. Food Sci.* **1988**, *53*, 1444–1447.
- Bullard, R. W.; Holguin, G. Volatile components of unprocessed rice (*Oryza sativa* L.). *J. Agric. Food Chem.* **1977**, *25*, 99–103.
- Burford, M. D.; Bartle, K. D.; Hawthorne, S. B. Directly coupled (on-line) SFE-GC: instrumentation and applications. *Adv. Chromatogr.* **1997**, *37*, 163–204.



- Buttery, R. G.; Ling, L. C. Volatile flavor components of corn tortillas and related products. *J. Agric. Food Chem.* **1995**, *43*, 1878–1882.
- Buttery, R. G.; Ling, L. C. Additional studies on flavor components of corn tortilla chips. *J. Agric. Food Chem.* **1998**, *46*, 2764–2769.
- Buttery, R. G.; Ling, L. C.; Juliano, B. O.; Turnbaugh, J. G. Cooked rice aroma and 2-acetyl-1-pyrroline. *J. Agric. Food Chem.* **1983**, *31*, 823–826.
- Buttery, R. G.; Stern, D. J.; Ling, L. C. Studies on flavor volatile of some sweet corn products. *J. Agric. Food Chem.* **1994**, *42*, 791–795.
- Buttery, R. G.; Stern, D. J.; Ling, L. C. Studies on flavour volatiles of some sweet corn products. *J. Agric. Food Chem.* **1997a**, *45*, 791–795.
- Buttery, R. G.; Ling, L. C.; Stern, D. J. Studies on popcorn aroma and flavor volatiles. *J. Agric. Food Chem.* **1997b**, *45*, 837–843.
- Catterick, T.; Craston, D.; King, B.; Walker, R. F.; Webb, K. S. Some recent developments in reference methodology within the United Kingdom. *Accredit. Qual. Assur.* **1999**, *4*, 3–13.
- Chang, S. S.; Vallese, F. M.; Huang, L. S.; Hsieh, O. A. L.; Min, D. B. S. Apparatus for the isolation of trace volatile constituents from foods. *J. Agric. Food Chem.* **1977**, *25*, 450–455.
- Chang, C. Y.; Seitz, L. M.; Chambers, E. Volatile flavor components of breads made from hard red winter wheat and hard white winter wheat. *Cereal Chem.* **1995**, *72*, 237–242.
- Chen, W. J. L.; Anderson, J. W. Effects of plant fiber in decreasing plasma total cholesterol and increasing high-density lipoprotein cholesterol. *Proc. Soc. Exp. Biol. Med.* **1979**, *162*, 310–313.
- Clawson, A. R.; Linforth, R. S. T.; Ingham, K. E.; Taylor, A. J. Effect of hydration on release of volatiles from cereal foods. *Lebensm. Wiss. Tehnol.* **1996**, *29*, 158–162.
- Coleman, W. M. A study of the behavior of polar and nonpolar solid-phase microextraction fibers for the extraction of Maillard reaction products. *J. Chromatogr. Sci.* **1997**, *35*, 245–258.
- Collins, F. W. Oat phenolics: structure, occurrence and function. In *Oats: Chemistry and Technology*; Webster, F. H., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1986; pp 227–295.
- Conway, W. D. *Counter-current Chromatography—Apparatus, Theory and Applications*; VCH: Weinheim, Germany, 1990.
- Coulibaly, K.; Jeon, I. J. An overview of solid-phase extraction of food flavor compounds and chemical residues. *Food Rev. Int.* **1996**, *12*, 131–151.
- da Silva, M. A. A. P. Flavor properties and stability of a corn-based snack: aroma profiles by gas chromatography (GC), GC-olfactometry, mass spectrometry, and descriptive sensory analysis. *Diss. Abstr. Int. B* **1994**, *54*, 4461.
- Debievre, P.; Peiser, H. S. Basic equations and uncertainties in isotope dilution mass spectrometry for traceability to SI of values obtained by this primary method. *Fresenius' J. Anal. Chem.* **1997**, *359*, 523–525.
- de Leon, A. A. Use of univariate and multivariate statistical procedures on quantitative descriptive sensory data (statistical procedures). *Diss. Abstr. Int. B* **1994**, *55*, 8.
- Dimberg, L. H.; Theander, O.; Lingnert, H. Avenanthramides—a group of phenolic antioxidants in oats. *Cereal Chem.* **1993**, *70*, 637–641.
- Dimberg, L. H.; Molteberg, E. L.; Solheim, R.; Frølich, W. Variation in oat groats due to variety, storage and heat treatment. I. Phenolic compounds. *J. Cereal Sci.* **1996**, *24*, 263–272.
- Durkee, A. B.; Thivierge, P. A. Ferulic acid and other phenolics in oat seeds (*Avena sativa* L. var Hinoat). *J. Food Sci.* **1977**, *42*, 551–552.
- Ekstrand, B.; Gangby, I.; Åkesson, G. Lipase activity in oats—distribution, pH dependence, and heat inactivation. *Cereal Chem.* **1992**, *69*, 379–381.
- Ekstrand, B.; Gangby, I.; Åkesson, G.; Stöllman, U.; Lingnert, H.; Dahl, S. Lipase activity and development of rancidity in oats and oat products related to heat treatment during processing. *J. Cereal Sci.* **1993**, *17*, 247–254.
- Elmore, J. S.; Erbahadir, M. A.; Mottram, D. S. Comparison of dynamic headspace concentration on Tenax with solid-phase microextraction for the analysis of aroma volatiles. *J. Agric. Food Chem.* **1997**, *45*, 2638–2641.
- El-Saharty, Y. S.; Tawakkol, M. S.; El-Zeany, B. A.; Berger, R. G. Odour active compounds of fresh wheat germ. *Adv. Food Sci.* **1997**, *19*, 90–94.
- Espinosa-Diaz, M.; Seuvre, A. M.; Voilley, A. Influence of physicochemical properties of aroma compounds on their interactions with other constituents. In *Flavour Science: Recent Developments*; Taylor, A. J., Mottram, D. S., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1996; pp 442–445.
- Fay, L. B.; Blank, I.; Cerny, C. Tandem mass spectrometry in flavour research. In *Flavour Science: Recent Developments*; Taylor, A. J., Mottram, D. S., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1996; pp 271–276.
- Folkes, D. J.; Gramshaw, J. W. The flavor and volatile of wheat bread crust. *Prog. Food Nutr. Sci.* **1981**, *5*, 369–376.
- Fors, S. M.; Schlich, P. Flavour composition of oil obtained from crude and roasted oats. *ACS Symp. Ser.* **1989**, *No. 409*, 121–131.
- Forss, D. A. Odor and flavor compounds from lipids. In *Progress in Chemistry of Fats and Other Lipids*; Holman, R. T., Ed.; Pergamon Press: New York, 1972; Vol. 13, pp 181–258.
- Frey, K. J.; Hammond, E. G. Genetics, characteristics, and utilization of oil in caryopses of oat species. *J. Am. Oil Chem. Soc.* **1975**, *52*, 358–362.
- Fritsch, C. W.; Gale, J. A. Hexanal as a measure of rancidity in low fat foods. *J. Am. Oil Chem. Soc.* **1977**, *54*, 225–228.
- Gansmann, W.; Vorwerck, K. Oat milling, processing and storage. In *The Oat Crop*; Welch, R. W., Ed.; Chapman and Hall: London, U.K., 1995; pp 369–408.
- Grosch, W. Determination of potent odourants in foods by aroma extract dilution analysis (AEDA) and calculations of odour activity values (OAVs). *Flavour Fragrance J.* **1994**, *9*, 147–158.
- Grosch, W.; Schieberle, P. Flavour of cereal products—a review. *Cereal Chem.* **1997**, *74*, 91–97.
- Guadagni, D. G.; Okano, S.; Buttery, R. G.; Burr, H. K. Correlation of sensory and gas-liquid chromatographic measurements of apple volatiles. *Food Technol.* **1966**, *20*, 166–169.
- Guth, H.; Grosch, W. Odorants of extrusion products of oat meal—changes during storage. *Z. Lebensm. Unters. Forsch.* **1993**, *196*, 22–28.
- Guth, H.; Grosch, W. Aromastoffe in Haferextrudaten (Flavour compounds in oat extrudates). *Getreide, Mehl Brot* **1994**, *48*, 50–52; FSTA 95-05-M0053.
- Hau, M. Y. M.; Hibberd, S.; Taylor, A. J. Modelling the uptake of diacetyl in extruded starch. In *Flavour Science: Recent Developments*. Taylor, A. J., Mottram, D. S., Eds., Royal Society of Chemistry: Cambridge, 1996, 437–441.
- Heydanek, M. G.; McGorin, R. J. Gas chromatography—mass spectroscopy investigations on the flavor chemistry of oat groats. *J. Agric. Food Chem.* **1981a**, *29*, 950–954.
- Heydanek, M. G.; McGorin, R. J. Gas chromatography—mass spectroscopy identification of volatiles from rancid oat groats. *J. Agric. Food Chem.* **1981b**, *29*, 1093–1095.
- Heydanek, M. G.; McGorin, R. J. Oat flavour chemistry: principles and prospects. In *Oats: Chemistry and Technology*; Webster, F. H., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1986; pp 335–369.
- Heymann, H.; Nobel, A. C.; Boulton, R. B. Analysis of methoxy-pyrazines in wines. 1. Development of a quantitative procedure. *J. Agric. Food Chem.* **1986**, *34*, 268–271.
- Hironaka, Y. Relationships between sensory flavor evaluation and gas chromatographic profiles of French bread. *Cereal Chem.* **1986**, *63*, 369–372.
- Hodge, J. E.; Mills, F. D.; Fisher, B. E. Compounds of Browning Flavor Derived from Sugar-Amine Reactions. *Cereal Sci. Today* **1972**, *17*, 34–40.



- Hornstein, I., Ed. *Flavor Chemistry*; American Chemical Society: Washington, DC, 1966; p vii.
- Hrdlicka, J.; Janicek, G. Carbonyl compounds in toasted oat flakes. *Nature* **1964a**, *201*, 1223.
- Hrdlicka, J.; Janicek, G. Volatile amines as components of toasted oat flakes. *Nature* **1964b**, *204*, 1201.
- Huang, C. J.; Zayas, J. F. Phenolic acid contributions to taste characteristics of corn germ protein flour products. *J. Food Sci.* **1991**, *56*, 1308–1315.
- Huang, C. J.; Zayas, J. F. Aroma characteristics of corn germ protein flours. *J. Food Sci.* **1996**, *61*, 258–261.
- Huang, T. C.; Bruechert, L. J.; Hartman, T. G.; Rosen, R. T.; Ho, C. T. The effect of lipids and carbohydrates on thermal generation of volatiles from commercial Zein. *J. Agric. Food Chem.* **1987**, *35*, 985–990.
- Ibañez, E.; Bernhard, R. A. Solid-phase microextraction (SPME) of pyrazines in model reaction systems. *J. Sci. Food Agric.* **1996**, *72*, 91–96.
- Karahadian, C.; Johnson, K. A. Analysis of headspace volatiles and sensory characteristics of fresh corn tortillas made from fresh masa dough and spray-dried masa flour. *J. Agric. Food Chem.* **1993**, *41*, 791–799.
- King, J. W. Integration of sample cleanup methods into analytical supercritical fluid extraction. *Am. Lab.* **1998a**, *30*, 46, 48, 50, 52, 54, 56, 58.
- King, J. W. Analytical supercritical fluid techniques and methodology: conceptualization and reduction to practice. *J. AOAC Int.* **1998b**, *81*, 9–17.
- Kirby, R. W.; Anderson, J. W.; Sieling, B.; Rees, E. D.; Chen, W. J.; Miller, R. E.; Kay, R. M. Oat-grain intake selectively lowers serum low-density lipoprotein cholesterol concentrations in hypercholesterolemic men. *Am. J. Clin. Nutr.* **1981**, *34*, 824–829.
- Klopfenstein, C. F.; Hosoney, R. C. Cholesterol-lowering effect of  $\beta$ -glucan-enriched bread. *Nutr. Rep. Int.* **1987**, *36*, 1091–1098.
- Kollengode, A. N. R.; Hanna, M. A. Flavor retention in pregelatinized and internally flavored starch extrudates. *Cereal Chem.* **1997**, *74*, 396–399.
- Labows, J. N.; Cagan, R. H. Complexity of flavor recognition and transduction. In *Food Flavor and Safety*; Spanier, A. M., Okai, H., Tamura, M., Eds.; American Chemical Society: Washington, DC, 1993.
- Laksanalamai, V.; Ilangantileke, S. Comparison of aroma compound (2-acetyl-1-pyrroline) in leaves from pandan (*Pandanus amaryllifolius*) and Thai fragrant rice (Khao Dawk Mali-105). *Cereal Chem.* **1993**, *70*, 381–384.
- Legendre, M. G.; Dupuy, H. P.; Ory, R. L.; McIlrath, W. O. Instrumental analysis of volatiles from rice and corn products. *J. Agric. Food Chem.* **1978**, *26*, 1035–1038.
- Likens, S. T.; Nickerson, G. B. Detection of hop oil constituents. *Proc. Am. Soc. Brew. Chem.* **1964**, 5–13.
- Litchev, V. Influence of oxidation processes on the development of the taste and flavor of wine distillates. *Am. J. Enol. Vitic.* **1989**, *40*, 31–35.
- Liukkonen, K. H.; Montfoort, A.; Laakso, S. V. Water-induced lipid changes in oat processing. *J. Agric. Food Chem.* **1992**, *40*, 126–130.
- Maga, J. A.; Lorentz, K. Taste threshold values for phenolic acids which can influence flavour properties of certain flours, grains and oilseeds. *Cereal Sci. Today* **1973**, *18*, 326–328, 350.
- Marsili, R. *Techniques for Analyzing Food Aroma*; Dekker: New York, 1997.
- Matlashewski, G. J.; Urquhart, A. A.; Sahasrabudhe, M. R.; Altosaar, I. Lipase activity in oat flour suspensions and soube extracts. *Cereal Chem.* **1982**, *59*, 418–422.
- Mauron, J. The Maillard reaction in food: A critical review from the nutritional standpoint. *Prog. Food Nutr. Sci.* **1981**, *5*, 5–35.
- Molteberg, E. L.; Magnus, E. M.; Bjørge, J. M.; Nilsson, A. Sensory and chemical studies of lipid oxidation in raw and heat-treated oat flours. *Cereal Chem.* **1996a**, *73*, 579–587.
- Molteberg, E. L.; Solheim, R.; Dimberg, L. H.; Frølich, W. Variation in oat groats due to variety, storage and heat treatment. II. Sensory quality. *J. Cereal Sci.* **1996b**, *24*, 273–282.
- Moon, H. I.; Lee, J. H.; Lee, D. J. Analysis of volatile flavour components in aromatic rices using electronic nose system. *Korean J. Crop Sci.* **1996**, *41*, 672–677; FSTA 97-10-M0067.
- Mulders, E. J.; ten Noever de Brauw, M. C.; Van Straten, S. Odor of white bread. II. Identification of components in pentane-ether extracts. *Z. Lebensm. Unters. Forsch.* **1973**, *150*, 306–310.
- Murray, K. E.; Shipton, J.; Whitfield, F. B.; Last, J. H. The volatiles of off-flavoured unblanched green peas (*Pisum sativum*). *J. Sci. Food Agric.* **1976**, *27*, 1093–1099.
- Nitz, S.; Kollmannsberger, H.; Drawert, F. Determination of sensorial active trace compounds by multidimensional gas chromatography combined with different enrichment techniques. *J. Chromatogr.* **1989**, *471*, 173–185.
- O'Conner, J.; Perry, H. J.; Harwood, J. L. A comparison of lipase activity in various cereal grains. *J. Cereal Sci.* **1992**, *16*, 153–163.
- Okada, K. Studies on the flavour of wheat flour. I. Flavour of wheat gluten (1). *J. Agric. Chem. Soc. Jpn.* **1969**, *43*, 675–681; FSTA 70-03-M0209.
- Pawliszyn, J. *Solid-Phase Microextraction: Theory and Practice*; Wiley-VCH: New York, 1997.
- Penton, Z. E. Sample preparation for gas chromatography with solid-phase extraction and solid-phase microextraction. *Adv. Chromatogr.* **1997**, *37*, 205–236.
- Petrov, M.; Danzart, M.; Giampaoli, P.; Faure, J.; Richard, H. Rice aroma analysis—discrimination between a scented and a nonscented rice. *Sci. Aliments* **1996**, *16*, 347–360.
- Pfannhauser, W. Volatile compounds during the extrusion cooking of a wheat-barley cross. *Dtsch. Lebensm. Rundsch.* **1990**, *86*, 69–72.
- Pfannhauser, W. Volatiles formed during extrusion cooking of cereals. *Flavour Fragrance J.* **1993**, *8*, 109–113.
- Rektorik, J. Method and device for gas-chromatographic analysis, and its application. Eur. Patent Appl. **1983**, *73*, 176–186.
- Richard-Molard, D.; Nago, M. C.; Drapron, R. Influence of the breadmaking method on French bread flavor. *Baker's Dig.* **1979**, *53*, 34–38.
- Roberts, D. D.; Pollien, P. Analysis of aroma release during microwave heating. *J. Agric. Food Chem.* **1997**, *45*, 4388–4392.
- Ropkins K.; Taylor, A. J. The isolation of flavour compounds from foods by enhanced solvent extraction methods. In *Flavour Science: Recent Developments*; Taylor, A. J., Mottram, D. S., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1996; pp 297–300.
- Rychlik, M.; Grosch, W. Identification and quantification of potent odorants formed by toasting of wheat bread. *Lebensm. Wiss. Technol.* **1996**, *29*, 515–525.
- Schieberle, P. Primary odorants in popcorn. *J. Agric. Food Chem.* **1991**, *39*, 1141–1144.
- Schieberle, P. Quantitation of important roast-smelling odorants in popcorn by stable isotope dilution assays and model studies on flavor formation during popping. *J. Agric. Food Chem.* **1995**, *43*, 2442–2448.
- Schieberle, P.; Grosch, W. Identification of the volatile flavor compounds of wheat bread crust—comparison with rye bread crust. *Z. Lebensm. Unters. Forsch.* **1985**, *180*, 474–478; *Chem Abst.* **1985**, 121993e.
- Schieberle, P.; Grosch, W. Potent odorants of the wheat bread crumb. Differences from the crust and effect of a longer dough fermentation. *Z. Lebensm. Unters. Forsch.* **1991**, *192*, 130–135.
- Schultz, T. H.; Flath, R. A.; Mon, T. R.; Egging, S. B.; Teranishi, R. Isolation of volatile components from a model system. *J. Agric. Food Chem.* **1977**, *25*, 446–449.
- Semwal, A. D.; Sharma, G. K.; Arya, S. S. Flavour degradation in dehydrated convenience foods—Changes in carbonyls in quick-cooking rice and Bengalgram dhal. *Food Chem.* **1996**, *57*, 233–239.

- Shen, G.; Hosoney, R. C. Comparisons of aroma extracts of heat-treated cereals. *Lebensm. Wiss. Technol.* **1995**, *28*, 208–212.
- Sjövall, O.; Lapveteläinen, A.; Johansson, A.; Kallio, H. Analysis of volatiles formed during oxidation of extruded oats. *J. Agric. Food Chem.* **1997**, *45*, 4452–4455.
- Smith, E. A.; Chambers, E., IV; Colley, S. Development of vocabulary and references for describing off-odors in raw grains. *Cereal Foods World* **1994**, *39*, 495–499.
- Sosulski, F.; Krygier, K.; Hogge, L. Free, esterified, and insoluble-bound phenolic acids. 3. Composition of phenolic acids in cereal and potato flours. *J. Agric. Food Chem.* **1982**, *30*, 337–340.
- Springett, M. B. An assessment of volatile trapping and concentration techniques: The effect of trapping time on the interpretation of food flavour chromatograms. In *Flavors and Off-flavors*; Charalambous, G., Ed.; Elsevier: Amsterdam, The Netherlands, 1990; pp 331–342.
- Stalcup, A. M.; Ekborg, K. H.; Gasper, M. P.; Armstrong, D. W. Enantiomeric separation of chiral components reported to be in coffee, tea, or cocoa. *J. Agric. Food Chem.* **1993**, *41*, 1684–1689.
- Sugawara, E.; Saiga, S.; Kobayashi, A. Relationships between aroma compounds and sensory evaluation of miso. *J. Jpn. Soc. Food Sci. Technol. (Nippon Shokuhin Kogyo Gakkaishi)* **1992**, *39*, 1098–1104; FSTA 93-07-M0021.
- Sugisawa, H.; Chen, C.; Naberta, K. Simultaneous distillation adsorption and its application. In *Analysis of Volatiles*; Schrier, P., Ed.; de Gruyter: New York, 1984; pp 357–369.
- Tai, T. L.; Chung, M. W.; Yi, J. L. Studies on the volatile compounds in cooked rice. *Food Sci. Taiwan* **1996**, *23*, 767–778; FSTA 97-05-M0042.
- Talou, T.; Sanchez, J. M.; Bourrounet, B. New trends in electronic noses for flavour chemistry. In *Flavour Science: Recent Developments*; Taylor, A. J., Mottram, D. S., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1996; pp 277–282.
- Tanchotikul, U.; Hsieh, T. C. Y. An improved method for quantification of 2-acetyl-1-pyrroline, a “popcorn”-like aroma, in aromatic rice by high-resolution gas chromatography/mass spectrometry/selected ion monitoring. *J. Agric. Food Chem.* **1991**, *39*, 944–947.
- Teranishi, R. New trends and developments in flavor chemistry. In *Flavor Chemistry—Trends and Development*; Teranishi, R., Buttery, R. G., Shahidi, F., Eds.; American Chemical Society: Washington, DC, 1989; pp 1–3.
- Uhlig, J. W.; Chang, A.; Jen, J. J. Effect of phthalides on celery flavor. *J. Food Sci.* **1987**, *52*, 658–660.
- Ullrich, F.; Grosch, W. Identification of the most intense volatile flavor compounds formed during autoxidation of linoleic acid. *Z. Lebensm. Unters. Forsch.* **1987**, *184*, 277–282.
- Urquhart, A. A.; Brumell, C. A.; Altosaar, I.; Matlashewski, G. J.; Sahasrabudhe, M. R. Lipase activity in oats during maturation and germination. *Cereal Chem.* **1984**, *61*, 105–108.
- Valcarcel, M.; Tena, M. T. Applications of supercritical fluid extraction in food analysis. *Fresenius' J. Anal. Chem.* **1997**, *358*, 561–573.
- Verhoeven, H.; Beuerle, T.; Schwab, W. Solid-phase microextraction: artifact formation and its avoidance. *Chromatographia* **1997**, *46*, 63–66.
- Wetzel, D. L.; Pussayanawin, V.; Fulcher, R. G. Determination of ferulic acid in grain by HPLC and microspectrofluorometry. *Dev. Food Sci.* **1988**, *17*, 409–428.
- Withycombe, D. A.; Lindsay, R. C.; Stuiber, D. A. Isolation and identification of volatile components from wild rice grain (*Zizania aquatica*). *J. Agric. Food Chem.* **1978**, *26*, 816–822.
- Yajima, I.; Yanai, T.; Nakamura, M.; Sakakibara, H.; Habu, T. Volatile flavor compounds of cooked rice. *Agric. Biol. Chem.* **1978**, *42*, 1229–1233.
- Yajima, I.; Yanai, T.; Nakamura, M.; Sakakibara, H.; Uchida, H.; Hayashi, K. Volatile compounds of boiled buckwheat flour. *Agric. Biol. Chem.* **1983**, *47*, 729–738.
- Yang, X. G.; Peppard, T. Solid-phase microextraction for flavor analysis. *J. Agric. Food Chem.* **1994**, *42*, 1925–1930.
- Youngs, V. L. Oat lipids and lipid-related enzymes. In *Oats: Chemistry and Technology*; Webster, F. H., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1986; pp 205–226.
- Zehentbauer, G.; Grosch, W. Apparatus for quantitative head-space analysis of the characteristic odorants of baguettes. *Z. Lebensm. Unters. Forsch.* **1997**, *205*, 262–267.
- Zehentbauer, G.; Grosch, W. Crust aroma of baguettes. I. Key odorants of baguettes prepared in two different ways. *J. Cereal Sci.* **1998a**, *28*, 81–92.
- Zehentbauer, G.; Grosch, W. Crust aroma of baguettes. II. Dependence of the concentrations of key odorants on yeast level and dough processing. *J. Cereal Sci.* **1998a**, *28*, 93–96.
- Zhou, M. X.; Robards, K.; Glennie-Holmes, M.; Helliwell, S. Structure and pasting properties of oat starch. *Cereal Chem.* **1998**, *75*, 273–281.
- Zhou, M. X.; Robards, K.; Glennie-Holmes, M.; Helliwell, S. Contribution of volatiles to the flavor of oatmeal. *J. Agric. Food Chem.* **1999**, submitted for publication.

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