Use of Fiber Interface Direct Mass Spectrometry for the Determination of Volatile Flavor Release from Model Food Systems

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Described in this paper is a fiber interface direct headspace mass spectrometric system for the real-time measurement of flavor release. The system was optimized for the detection of the garlic aroma volatile, diallyl disulfide, from water. Parameters investigated included interface temperature, flow rate through the fiber, flow rate through the sample vessel, and sample stir rate. The delay time for detection of sample after introduction into the sample vessel was determined as 43 s. The system proved to be reliable and robust with no loss in sensitivity or contamination of the mass spectrometer over a 6 month period. The technique was applied to a homologous series of aliphatic alcohols from C_2 to C_7. Results showed that as polarity decreased with increasing chain length the release of volatile into the headspace was faster and gave a higher maximum intensity. Release of the garlic aroma volatile from different commercial mayonnaise products clearly showed a decrease in the release of diallyl disulfide as fat content increased. These results demonstrate the potential of using this technique as a tool for understanding the complex interactions that occur between flavor compounds and the bulk food matrix.

Keywords: *Fiber interface; dynamic headspace; flavor release; diallyl disulfide; mayonnaise; garlic; volatile; mass spectrometry*

INTRODUCTION

Release of flavor during eating is a key quality parameter in the determination of consumer preference for food and drink types, brands, etc. There are many factors that can influence this release such as the physicochemical properties of the flavor compounds, the concentrations of the flavor components, and their interaction with the nonvolatile compounds which make up the matrix of the foods. Consumer demands for new products, in particular reduced-fat foods, which are considered to be more healthy, can lead to products that have atypical flavor release properties. The development of successful new products with the correct balance and release of flavor components requires understanding of the complex series of interactions that occur during the eating process. Only the compounds released from the food in sufficiently high concentrations during eating will stimulate the olfactory system and be perceived as a flavor. The parameters regarding composition and breakdown of foods affecting the release of flavor have been recently reviewed (Bakker, 1995).

The development of time−intensity analysis has been recently reviewed by Cliff and Heymann (1993). This technique can be used to determine the release and perception of flavor from complex food matrixes. Time−intensity measurements are an extension of the scaling method in use for quantitative descriptive analysis and consist of the continuous scaling of perceived intensity of an attribute, until the perceived attribute intensity has dropped to zero or the recording period has stopped. This information is considered important because not only the concentration of volatile compounds released is important for sensory perception, but the time required for release is of importance for the perception of a well-balanced flavor. Time−intensity measurements give information regarding maximum intensity, the start time of the stimulus perception, the time needed to reach maximum intensity, total duration of the stimulus, and area under the curve. Other parameters such as rate of appearance, rate of extinction, or drop in intensity relative to first introduction can also be derived (Lee, 1986). However, sensory time−intensity measurements are time-consuming and expensive. The stimulus concentration released from foods cannot be separated from the perceptual processes of the assessors. Hence, an instrumental method to measure flavor release from foods as a function of time is an essential prerequisite to determine the effect of the food matrix on the flavor stimulus concentration.

Instrumental methods offer the potential of a routine and rapid measure of flavor release curves. Several types of methods have been applied to these analyses, including the analysis of breath from subjects during eating (Soeting and Heidema, 1988; Linforth and Taylor, 1993). These methods measure a combination of flavor released from the food matrix and the perceptual differences between subjects, and thus this type of data contains information regarding the release of the flavor from the foods as well as the person-to-person variation, which includes perception differences due to eating habits, sensitivity, degree of sensory fatigue, etc. Clearly, using the mouth as the vessel for flavor release is important as this is the point at which all food flavors are ultimately judged. However, when information regarding matrix/flavor interactions is being investigated, the large inter- and intravariations that arise

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using consumers can mask sample effects. Also, sample palatability and safety are important issues when using consumers. These issues are resolved to a large degree using a model vessel in place of the human subject. A number of authors have developed methods for the measurement of release from model vessels that simulate the mouth conditions (Lee, 1986; Roberts and Acree, 1995; Elmore and Langley, 1996; Roberts et al., 1996). Using model vessels allows the determination of selected flavor release curves as a function of time in a repeatable analytical system, giving information with regard to the factors that can affect flavor release and greatly enhancing the capability of designing new products with specified flavor release characteristics.

Roberts and Acree (1995) developed a device based on a modified blender that simulated the mouth/nose system, connected to a headspace trapping system. With this they investigated the effects of saliva, temperature, shearing, and oil on flavor release. Bakker et al. (1998) described a model system from which the dynamic release of flavor from the model food into the air was determined by headspace sampling with a syringe, a rather time-consuming method. The release of flavor from liquid gelatin models as a function of shear rate and gelatin concentration was determined, and these data were used to model the effects of shear and viscosity on the mass transfer coefficient at the liquid−air interphase, which they concluded was the parameter determining the release rate. Other model vessels have been developed that are directly linked to a mass spectrometer allowing dynamic measurement of release curves. Various interface systems have been tested, such as a jet separator, an enrichment technique based on the differential diffusion of solute and carrier gas after the effluent has passed through a small jet into a vacuum (Elmore and Langley, 1996; Roberts et al., 1996). However, this method was rather cumbersome to use for flavor release studies.

Interfacing where the headspace or nosespace is introduced directly into the into the mass spectrometer has also been tried (Lee, 1986; Linforth and Taylor, 1993), but these methods suffer from contamination of source and poor sensitivity. Soeting and Heidema (1988) used a membrane separator, which consisted of a small area of silicone membrane, allowing short response times. This method was set up with an air flow of breath past the membrane, with the vacuum of the mass spectrometer providing the driving force for diffusion. The efficiency of such a system will depend on the maintenance of a high concentration gradient over the membrane. Atmospheric pressure ionization mass spectrometry for breath analysis was first used by Benoit et al. (1983), by developing a special breath inlet system allowing the direct sampling of exhaled human breath. Some of these methods could easily be adapted to determine flavor release in model systems.

Described here is a system using a stirred, jacketed vessel connected to a benchtop EI mass spectrometer via a fiber interface, which allows the measurement of flavor released from the sample in the vessel in real time, with a only small time delay, which was calculated. The setup is based on the helium-purged hollow fiber membrane mass spectrometer used for the continuous measurement of organic compounds in water (Slivon et al., 1991). Included in this paper are the results of varying the system parameters on optimizing the detection of diallyl disulfide. Using the optimized parameters, the release curves of a homologous series of aliphatic alcohols from aqueous solutions were determined and the release curves of diallyl disulfide from three commercial mayonnaises were also measured.

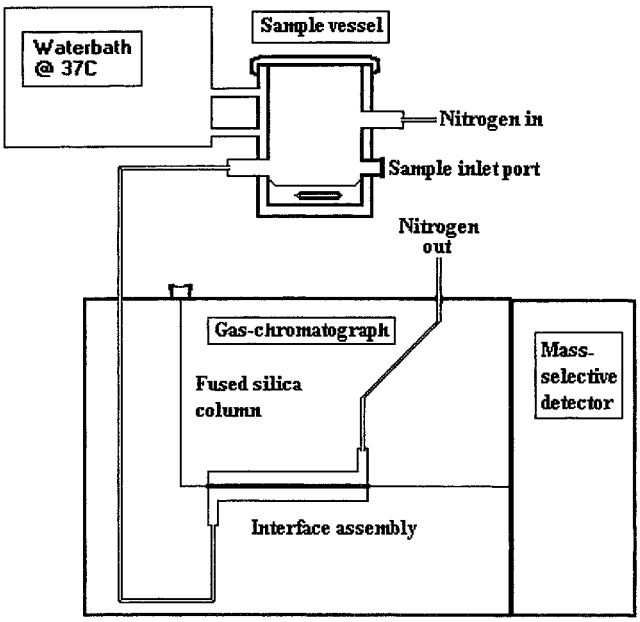

Figure 1. Schematic diagram of the overall FIDH-MS system.

MATERIALS AND METHODS

Ethanol, pentan-1-ol, and heptan-1-ol were of Analar grade purchased from Merck Ltd. (Poole, Dorset, U.K.). Butan-1-ol and hexan-1-ol were >98% pure and purchased from Sigma-Aldrich Co. Ltd. (Poole, Dorset, U.K.). Propan-1-ol was >99.5% pure and supplied by Fluorochem Ltd. (Glassop, U.K.). Diallyl disulfide was >85% pure and supplied by R. Kubec, Institute of Chemical Technology, Czech Republic.

Mass spectrometry was carried out on a Hewlett-Packard 6890 series gas chromatograph connected to an HP 5973 mass-selective detector. Sample vessel and glassware for the fiber interface direct mass spectrometry (FIDH) system were made by J. Young (Scientific Glassware) Ltd., London, U.K. Figure 1 shows a schematic diagram of the overall FIDH-MS system. The glass sample vessel was water-jacketed with a standard Pyrex 60 screw cap. It was fitted with a 15 mm septum sample injection port. Nitrogen inlet and outlet was through a 4 mm i.d. glass tube. The sample vessel was connected to the interface via 1 m of 3 mm i.d. PTFE tubing. Figure 2 shows a diagram of the interface. This was connected in the GC oven in place of the capillary column. The interface was connected to the injector port through 0.5 m of 100 μm fused silica, and similarly the interface was connected to the MS through 0.5 m of 100 μm fused silica. The interface itself was 100 mm × 30 mm with glass projections into the vessel to increase the turbulence as the sample vapor flows through the interface. The fiber was made of methyl silicone (Silastic RX50) supplied by Dow Chemical Co., 70 mm long, 0.305 mm i.d. × 0.635 mm o.d.

Determination of the Rate of Release of Diallyl Disulfide from Water. The sample vessel was held at 37 °C and connected with a nitrogen flow rate through the headspace that could be controlled between 0 and 500 mL min^{-1}. The vessel was flushed with nitrogen for a minimum of 5 min before the analysis was begun. At time zero the mass spectrometer was started and after 1 min, the sample, pre-equilibrated at 37 °C, was injected through the septum into the sample vessel. Except where specifically noted, all samples were 5 mL of a 50 ppm (v/v) diallyl disulfide in deionized water, pre-equilibrated at 37 °C for 30 min, and all were analyzed in triplicate. Mass spectral data were collected for 10 min. The

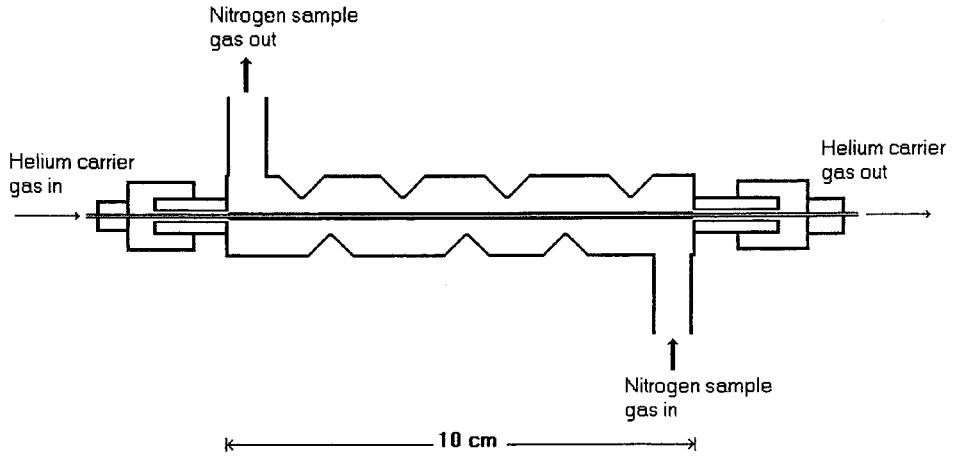

Figure 2. Diagram of the fiber interface.

interface was held in the GC oven. Interface temperature and helium flow through the fiber were varied using the normal GC controls (see below).

MS conditions were as follows: ionizing voltage, 70 eV; scan range, 40.2−300.0 amu; scan rate, 5.37 s^{-1}.

Because only single volatiles were added to the model system, resolution of different compounds was not an issue. However, the same technique could be used using selected ion monitoring, allowing the determination of a number of selected volatiles in a complex mixture, by focusing on mass ions typical for the volatiles of interest.

Optimization of FIDH-MS System Variables. Analyses were carried out in triplicate, as described above under Determination of the Rate of Release of Diallyl Disulfide from Water with the following exceptions.

(a) Determination of Delay Time. Twenty milliliters of a 1000 ppm (v/v) solution of diallyl disulfide in deionized water was placed in a 40 mL amber glass vial fitted with a "mininert" septum; this was allowed to equilibrate for 30 min at 37 °C. Two hundred microliters of headspace was injected into the sample vessel, and the time for the first mass fragments to be detected was determined. A 200 μL sample was also injected into the injection port of the GC, and again the time for the first mass fragments to be detected was determined.

(b) Interface Temperature. Values investigated were 40, 100, and 140 °C. For these experiments the sample flow rate was 58 mL min^{-1} and the helium carrier gas flow rate, 2 mL min^{-1}.

(c) Helium Flow Rate through the Fiber. Two helium flow rates were tested, 2 and 4 mL min^{-1}. For these experiments the interface temperature was set at 140 °C and sample flow rate at 58 mL min^{-1}.

(d) Sample Vessel Flow Rate. A range of nitrogen flow rates through the vessel were tested; these were 21, 29, 38, 48, 58, 101, and 120 mL min^{-1}. Interface temperature was 140 °C and helium carrier gas flow rate, 2 mL min^{-1}.

(e) Sample Stir Rate. Samples were stirred using a 2 cm in diameter magnetic stirrer bar. Four settings were tested: no stirring and 6.2, 10.5, and 19.8 rev s^{-1} were determined using a Veeder-Root series 661, hand tachometer system. Interface temperature was 140 °C, sample carrier gas flow rate, 58 mL min^{-1}, and helium carrier gas flow rate, 2 mL min^{-1}. Duplicate analyses were carried out on each sample.

Determination of Release of a Series of Aliphatic Alcohols in Aqueous Solution. Using the optimized conditions from above, 5 mL of a 1000 ppm solution of different aliphatic alcohols pre-equilibrated at 37 °C was injected into the sample vessel of the FIDH-MS apparatus. Release curves were determined over a 15 min period. The alcohols tested were ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, and heptan-1-ol.

Determination of the Release Patterns for Diallyl Disulfide from a Range of Commercial Mayonnaise Products. Three commercial mayonnaise products were purchased locally. These were (1) Heinz Weightwatchers (1.6 g of protein, 9.7 g of carbohydrate, 9.5 g of fat per 100 g), (2) Hellmans light (0.7 g of protein, 6.1 g of carbohydrate, 29.8 g of fat per 100 g), and (3) Hellmans real (1.1 g of protein, 1.2 g of carbohydrate, 79.1 g of fat per 100 g). Mayonnaise (10 g), distilled water (10 g), and of diallyl disulfide (10 μL) were placed in a 40 mL glass vial fitted with a "mininert" septum. This was allowed to equilibrate at 37 °C for 1 h, after which time 10 mL was transferred to the sample vessel of the FIDH-MS. Data were collected for 15 min as previously described. Each type of mayonnaise was analyzed in triplicate.

RESULTS AND DISCUSSION

Optimization of FIDH-MS System Variables. The setup is simple and consists of a temperature-controlled vessel containing a stirred sample, an air flow over the sample to sweep the volatiles through the temperature-controlled hollow fiber interface, and a helium purge through the center of the fiber to transport the volatiles into the mass spectrometer. The sample is placed in the vessel with a syringe, while nitrogen is already sweeping through the vessel. To optimize the system for our experimental purpose, where our main interest is in studying factors affecting the release of flavor from the sample, the volatiles need to be detected with as little delay as possible and with maximum sensitivity. To optimize the system, each part of the process will need to be considered in turn.

The first step is partitioning of the volatile between the sample and the air. It is assumed that this flavor release process starts instantaneously when the sample is introduced into the sample vessel. The amount of flavor released in the air space will depend on the partition coefficient, air flow, temperature, and stirring rate (Bakker, 1995). Essentially in this vessel parameters simulating the release of flavor in the mouth are to be studied; hence, the temperature was kept constant at 37 °C. Once the released volatiles reach the hollow fiber, they pass through the fiber by the process of pervaporation. This occurs in three distinct phases. The first involves adsorption of the analyte onto the surface of the fiber, a process driven by the air−fiber partition coefficient. Providing the volatiles are soluble in the fiber material, they diffuse across the fiber under the force of a concentration gradient that exists through the thin layer of fiber material. Finally, the volatiles evaporate from the inner surface, under the influence of the reduced pressure in the mass spectrometer and the fiber−air (helium) partition coefficient, where they are swept into the mass spectrometer by the helium

carrier gas. A sufficient helium gas flow will ensure that the buildup of a stagnant layer on the inside of the fiber is avoided and the concentration of volatiles on the inside of the fiber approaches zero, thus maintaining a maximum concentration gradient across the fiber. The helium flow through the fiber leads to a more efficient transport of the volatiles into the mass spectrometer and ensures the fiber maintains its three-dimensional structure, which is more difficult to maintain in setups using only the vacuum system to introduce the sample into the mass spectrometer.

The recorded volatile concentration (abundance units) as a function of time has the general shape of a time−intensity curve. The curve consists of an initial slope of the curve, or initial release rate, followed by a plateau or I_{max} value, at which the amount released from the vessel is in equilibrium with the amount of volatile swept away by the air flow, followed by a decay curve, which indicates the concentration of the volatile in the sample is diminishing. When a larger sample is used, in which the concentration of volatiles is not rapidly exhausted in the liquid and therefore does not limit release into the headspace, a plateau could be achieved at which the release from the sample is in equilibrium with the amount swept away by the air flow. T_{max} is determined as the time at which the release curve reaches I_{max}.

(a) Delay Time. The total delay time (dt) from the sample vessel to the point of detection was determined as 43 s, determined as described under Materials and Methods. (Note the delay time also includes a time for the concentration of the analyte to reach the minimum detection level for the mass spectrometer.) This is made up from three components, shown in eq 1:

$$dt = dt1 + dt2 + dt3 \text{ (s)} \quad (1)$$

dt1 is the time required for the volatile to travel from the injection port of the sample vessel to the middle of the outer surface of the fiber interface. Because the release of flavor is assumed to start immediately, the time will depend on the architecture of the setup (volume, diameter of tubing, etc.) and the air flow and can be calculated for a given flow. Assuming that on injection some molecules of sample passed instantaneously across the sample vessel, the total path length from vessel to interface is 1.0 m. Assuming a diameter of 3 mm across the total path length at a flow rate of 58 mL min^{-1}, dt1 was calculated as ≈7 s.

dt2 is the time required for volatiles to pass through the fiber, which will depend on the concentration gradient, the temperature, and the thickness of the fiber. The effect of temperature is discussed in the next section, whereas the thickness of the fiber is kept constant. Delay time dt2 can be estimated from eqs 2a,b below:

$$dt2 = dt - (dt1 + dt3) \text{ (s)} \quad (2a)$$

$$dt2 = 43 - (7 + 1) = 35 \text{ (s)} \quad (2b)$$

dt3 is the time required for the volatile to reach the mass spectrometer from the inside of the hollow fiber, and determined as described under Materials and Methods, it can be calculated for a given flow, as half the time taken for the detection of the sample after injection into the GC injection port. It was determined as ≈1 s.

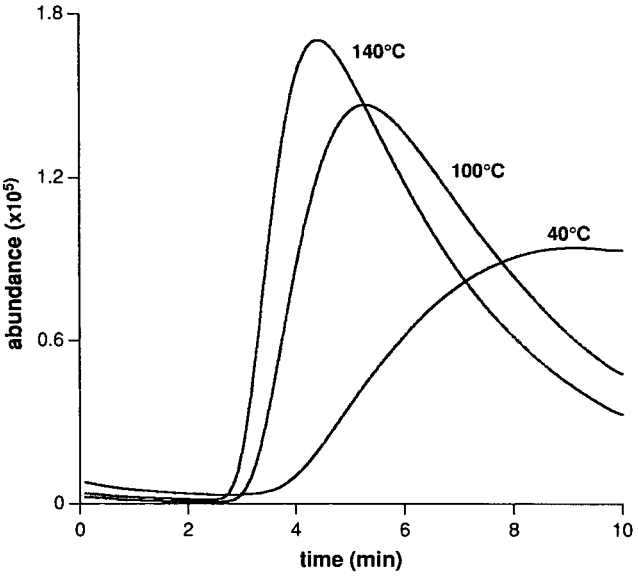

Figure 3. Average release curves ($n = 3$) for diallyl disulfide at interface temperatures of 40, 100, and 140 °C.

Table 1. Effect of Interface Temperature on the Time at Half-Maximum Intensity (t_{50}), Plateau Value (I_{max}) in Abundance Units (au), and Diffusion Coefficient (D) for the Movement of Diallyl Disulfide across the Fiber Interface[a]

interface temp (°C)	t_{50} (s)	SE	D ($\times 10^{-6}$) ($cm^2\ s^{-1}$)	SE ($\times 10^{-6}$)	I_{max} (au)	SE
40	212.32	2.24	0.72	0.0075	94196	1429
100	57.60	2.24	2.66	0.11	147680	2549
140	32.10	1.26	4.77	0.19	170603	433

[a] Results shown are the mean of three replicate determinations with standard error (SE).

It needs to be borne in mind that the detection limit as a function of the concentration in the liquid will also depend on the partition coefficients (sample−air and air−fiber) and the sensitivity of the mass spectrometer for specific compounds, because the volatile concentration in the air is actually determined. An increase in the affinity of the volatile for the fiber will enhance the detection.

(b) Interface Temperature. The release curves for diallyl disulfide from water (Figure 3) show that both I_{max} and T_{max} increased as the interface temperature increased from 40 to 140 °C. From these curves t_{50}, defined as the time to reach half the maximum intensity, can be readily determined using eq 3. This equation assumes that interface temperature affects only dt2, the time for diallyl disulfide to cross the fiber, while dt1 and dt3 remain constant.

$$t_{50} = (T_{max}/2) - (dt1 + dt3) \text{ (s)} \quad (3)$$

From this, the diffusion coefficient or diffusivity, D, can be determined according to eq 4 (Ziegel et al., 1969).

$$D = L2/(7.199t_{50}) \text{ } (cm^2\ s^{-1}) \quad (4)$$

D is a measure of the resistance of the fiber to the mass transfer of diallyl disulfide across the fiber, and L is the thickness of the fiber wall. The mean t_{50} and D values together with the standard error of those means (Table 1) show a lowering of the resistance of the fiber material to the mass transfer of diallyl disulfide as the interface temperature increases. Breakdown of the fiber material

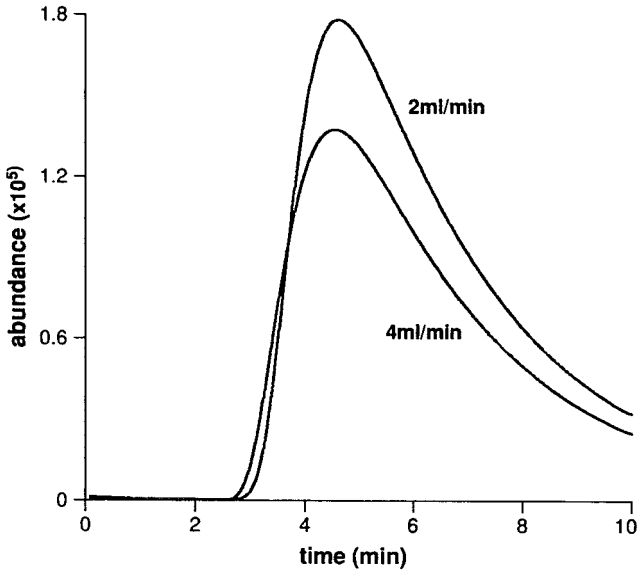

Figure 4. Average release curves ($n = 3$) for diallyl disulfide at helium flow rates of 2 and 4 mL min^{-1} through the fiber.

Table 2. Plateau Value (I_{max}) in Abundance Units (au) and Time To Reach Plateau Value (T_{max}) for Diallyl Disulfide at Helium Flow Rates of 2 and 4 mL min^{-1} through the Fiber[a]

flow rate through fiber (mL min^{-1})	I_{max} (au)	SE	T_{max} (min)	SE
2	178129	2201	3.6	0.03
4	137555	3693	3.6	0.05

[a] Results shown are the mean of three replicate determinations with standard error (SE).

occurs at temperatures >150 °C; hence, 140 °C was taken as the highest safe operating temperature and was used in all further analyses.

(c) Helium Flow Rate through the Fiber. Another parameter affecting the detection is helium carrier gas flow through the hollow fiber. Without helium flow, the efficiency is expected to be reduced, due to a buildup of concentration of volatile in the fiber space and possibly the formation of a boundary layer. Figure 4 shows the effect of helium carrier gas flow through the fiber. The constraints of the GC/MS system allowed only 2 and 4 mL min^{-1} to be investigated. The mean I_{max} value (Table 2) decreased when the flow rate increased, but there was no effect on T_{max}. Increasing flow rate will have a dilution effect on the concentration in the air, and this is likely to lead to the reduced I_{max} value. Therefore, 2 mL min^{-1} was used in subsequent analyses.

(d) Sample Vessel Flow Rate. The effect of the nitrogen flow rate, ranging from 21.4 to 120.0 mL min^{-1} through the sample vessel (Figure 5), shows clear differences on the release curves of diallyl disulfide. The low I_{max} value observed at the lowest flow rate (Table 3), 21 mL min^{-1}, may be due to insufficient mixing of the sample at the air−fiber interface, resulting in a stagnant layer with a depleted volatile concentration, thus resulting in a reduced response. Flow rates between 29 and 58 mL min^{-1} gave broadly the same I_{max}, indicating adequate mixing at the air−fiber interface. T_{max} generally decreased with increasing flow rate up to 100 mL min^{-1}. Under dynamic conditions the headspace is continually removed from the vessel, which unbalances the equilibrium and thus continually strips diallyl disulfide from the liquid phase. I_{max} in this case occurs when the rate of removal of diallyl disulfide from the liquid phase has

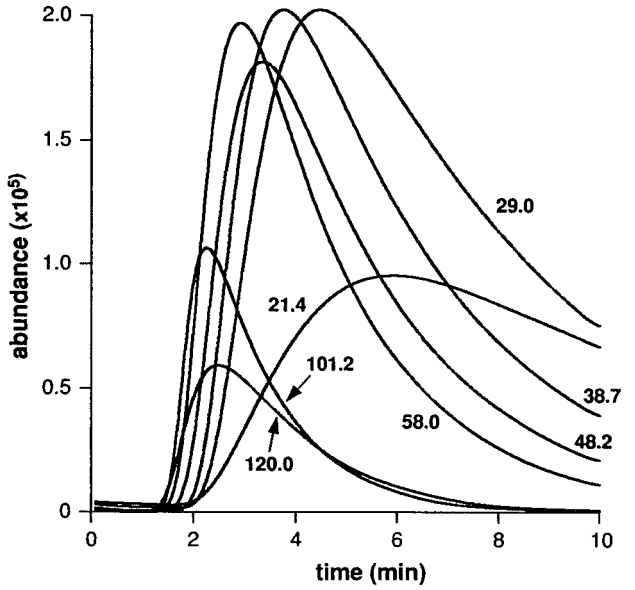

Figure 5. Average release curves ($n = 3$) for diallyl disulfide at sample vessel flow rates of 21.4, 29.0, 38.7, 48.2, 58.0, 101.2, and 120.0 mL min^{-1}.

Table 3. Plateau Value (I_{max}) in Abundance Units (au) and Time To Reach Plateau Value (T_{max}) for Diallyl Disulfide at Different Flow Rates through the Sample Vessel[a]

flow rate (mL min^{-1})	I_{max} (au)	SE	T_{max} (s)	SE
120	59240	3560	147.6	1.8
101	106760	6837	135.6	1.8
58	197755	633	174.6	4.2
48	181786	5670	199.8	3.6
38	202372	5063	224.4	1.8
29	202316	1957	268.8	1.8
21	95359	4479	356.4	7.2

[a] Results shown are the mean of three replicate determinations with standard error (SE).

reached a steady state. When the concentration of diallyl disulfide in the liquid is not limiting, the change in flow rate effectively results in a change in headspace volume, resulting in different times to reach equilibrium. However, the final concentration of diallyl disulfide in the headspace, at equilibrium, will be the same. This is borne out by the results between 29 and 58 mL min^{-1}, at which I_{max}, which is a measure of the headspace concentration at equilibrium, remains constant and the time to reach I_{max} (T_{max}) increases with increasing flow rate through the headspace.

At flow rates of 100 and 120 mL min^{-1}, the diallyl disulfide concentration in the liquid sample becomes limiting and the release curves show a rapid decay as diallyl disulfide is stripped from the sample. This results in a lower concentration of diallyl disulfide in the headspace because the liquid sample is depleted before the air−liquid equilibrium is established and the I_{max} values are lower.

(e) Effect of Stirring Rate. A series of experiments was carried out to determine the effect of stirring rate on diallyl disulfide release from aqueous solutions. A similar experiment has been reported in which the headspace was stirred to avoid any buildup of a concentration gradient but without any air flow through the headspace (Bakker et al., 1998). These authors reported that the initial release rate of diacetyl from an aqueous gelatin solution increased with an increase in the stirring rate, while the same equilibrium parti-

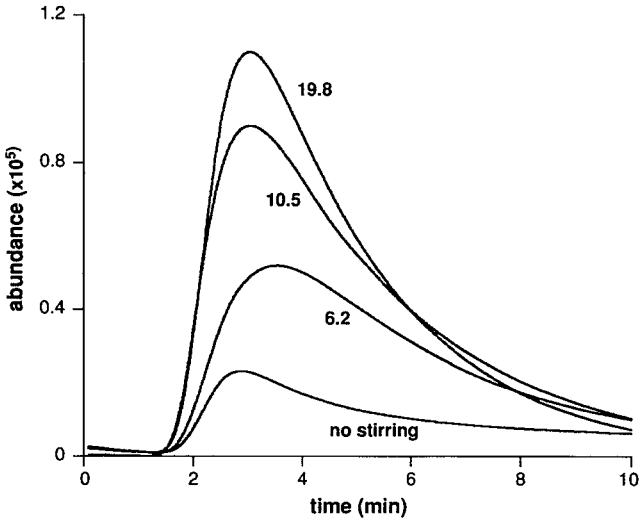

Figure 6. Average release curves ($n = 2$) for diallyl disulfide at sample stir rates of 0, 6.2, 10.5, and 19.8 rev s^{-1}.

Table 4. Plateau Value (I_{max}) in Abundance Units (au) and the Rate of Release Values of Diallyl Disulfide at Different Sample Stirring Rates[a]

stirring rate (rev min^{-1})	√stirring rate (rev min^{-1})	I_{max} (au)	range	rate of release (au min^{-1})	range
0	0	23190	±2757	24447	±1790
369	19.21	51840	±979	42126	±1606
632	25.13	89941	±4609	92228	±2927
1185	34.43	109995	±617	111484	±2049

[a] Results shown are the mean of two replicate determinations with range. There is a linear relationship between rate of release and stir rate (eq 5) and between rate of release and I_{max} (eq 6).

$$\text{rate of release} = 2588 \text{ stir rate} + 16611 \quad (R^2 = 0.84) \qquad (5)$$

$$\text{rate of release} = 1.05 I_{max} - 4317 \quad (R^2 = 0.98) \qquad (6)$$

tioning coefficient was reached for all stirring rates, although it took longer to establish with a slower stirring rate. Their results also showed that the release rate increased linearly with the square root of the stirring rate, as predicted by using a model based on the penetration theory (Coulson and Richardson, 1993). Figure 6 shows the time-dependent release curves of diallyl disulfide for stirring rates between 6.17 and 19.8 rev s^{-1} while there was a constant air flow over the sample. The square root of stirring rate, I_{max}, and rate of release of diallyl disulfide are listed in Table 4, and results show a linear relationship between release of diallyl disulfide and square root of stirring rate (see Table 4, eq 5). These results, obtained under dynamic conditions, are in agreement with the findings of Bakker et al. (1998) determined without an air flow. Under the dynamic conditions of this study, that is, with a continuous air flow over the sample, the I_{max} value does not reflect an equilibrium partition coefficient but expresses the balance between the amount of diallyl disulfide released into the headspace and the amount of diallyl disulfide swept away by the air flow. Hence, both rate of release and I_{max} would be expected to increase with an increase in stirring rate. This is shown by the excellent linear correlation ($R^2 = 0.98$) between rate of release and I_{max} (see Table 4, eq 6).

Determination of Release Curves of a Homologous Series of Aliphatic Alcohols from Aqueous Solutions. The release curves of a series of primary aliphatic alcohols (C_2−C_7 shows an increase in I_{max} and T_{max} with increasing molecular weight. The most important factor in the detection of the alcohols is mass transfer from the liquid phase into the headspace, influenced by both volatility and solubility of the alcohols. As carbon number increases, the alcohols become less polar and partition to a greater extent into the headspace, resulting in the increase in I_{max}. Air−water partition coefficients determined for primary alcohols and aliphatic alcohols between C_2 and C_6 at 25 °C range from 0.13×10^{-3} to 16×10^{-3} (Overbosch et al., 1991).It is clear that dynamic release follows a similar pattern, although the magnitude of the increase in release is different under dynamic conditions. It is also likely the alcohols will partition more readily into the hydrophobic fiber material as they decrease in polarity, again leading to an increase in I_{max}.

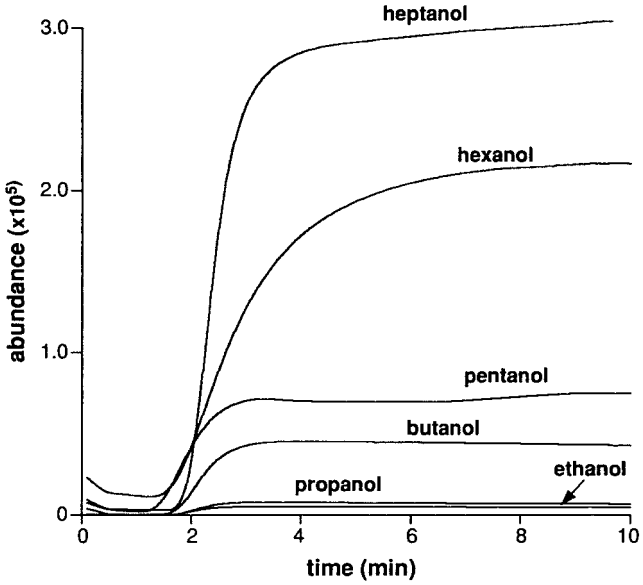

Figure 7. Average release curves ($n = 3$) from water for a range aliphatic alcohols, C_2−C_7.

Determination of the Release Curves for Diallyl Disulfide from a Range of Commercial Mayonnaise Products. The release curves for diallyl disulfide from three different commercial mayonnaises diluted 1:1 with water prior to analysis to facilitate stirring (Figure 8) show an increase in I_{max} with decreasing fat content. In the samples containing 14.9 and 39.5% fat, respectively, diallyl disulfide was detected only in low concentrations in headspace. These curves clearly demonstrate the importance of fats as carriers of generally hydrophobic flavor compounds. Perception of garlic from the lowest fat mayonnaise is likely to be much greater than in both medium- and high-fat mayonnaises at this concentration of flavoring.

Conclusions. System variables have been shown to have an effect on the detection of diallyl disulfide. Using the criteria of the highest I_{max} value and the shortest T_{max}, the optimal conditions were determined as follows: interface temperature, 140 °C; helium flow rate through fiber, 2 mL min^{-1}; nitrogen flow rate through the sample vessel, 58 mL min^{-1}; sample stirring rate, 19.8 rev s^{-1}. Applying this method to a series of aqueous solutions of aliphatic alcohols showed an increase in I_{max} with increasing carbon chain length. These results are consistent with an increased partition of the alcohols into the headspace with decreasing polarity. Also illustrated here are the release curves of garlic flavor from three mayonnaises, which clearly show an application of this system in the development of new products.

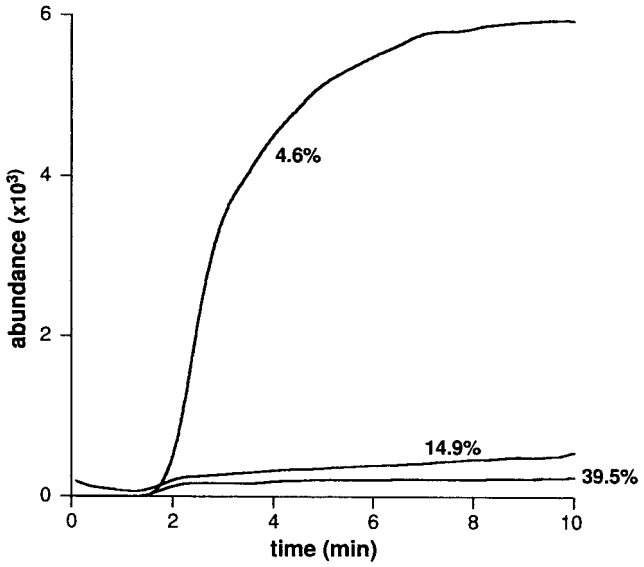

Figure 8. Average release curves ($n = 3$) for diallyl disulfide from commercial mayonnaise samples with fat levels of 4.6, 14.9, and 39.5%, expressed as percentage by weight after 1:1 dilution.

An understanding of the behavior of flavor compounds in different food matrixes is central to the development of successful foods and drinks. This FIDH-MS system, based on a simple modification of a benchtop GC/MS, provides a relatively inexpensive, simple, robust, and reproducible method for the measurement of release patterns from foods. The method can provide much more efficient information than direct headspace injections with a syringe (Bakker et al., 1998) and proved very much more reliable than the use of a jet separator (Elmore and Langley, 1996; Roberts et al., 1996). The hollow fiber setup allows a more efficient transfer of volatiles into the mass spectrometer than a flat membrane (Soeting and Heidema, 1988). System variables can be easily optimized to give a rapid response to different volatile organic compounds. Applications for this system are broad, providing a useful tool for the determination of interactions between flavor compounds and the food matrix, from which selected volatiles can be monitored using selected ion monitoring mode. This type of interface system also has the potential of being used in process control on-line to monitor the formation of certain volatiles during food manufacture, using continuous sampling of air. Further developments of the system to further improve sensitivity and response time are being carried out in the authors' laboratory, including sampling of liquids.

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