

# Use of the MS–Sensor to Discriminate between Different Dosages of Garlic Flavoring in Tomato Sauce

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A method has been developed to discriminate between different dosages of garlic flavoring in tomato sauce with the help of a mass spectrometry based sensory system. Four fragment ions  $m/z$  73, 81, 114, and 120 were selected as “sensor array” during direct injection of the sample headspace into the mass spectrometer. Tomato sauces blended with different types of flavoring could be discriminated, and concentration gradients could be monitored. Fragment ions were chosen after volatile components had been analyzed and identified by SPME-GC/MS and HS-GC/MS (full scan). HS-GC/MS profiles of  $m/z$  73, 81, 114, and 120 were recorded in the selected ion monitoring mode.

**Keywords:** *MS-sensor; mass spectrometry based sensor; dosage; garlic flavoring; pattern recognition*

## INTRODUCTION

Monitoring and controlling raw and finished goods are very important issues in the food industry. Classical analytical techniques such as gas chromatographic analysis (GC-FID), sniffing-GC-FID, GC/MS, sniffing-GC/MS, and/or HPLC analysis combined with sample preparation techniques such as solvent extraction or simultaneous steam distillation are routinely used for quality evaluation in laboratories today. These analytical techniques are, however, time-consuming and expensive, requiring workplaces equipped with a variety of different instruments and skilled personnel to interpret the analytical results.

It has thus become increasingly important to develop alternative analytical techniques that are rapid, robust, and simple to reduce per sample time investment and/or to conduct online analyses. This is why gas sensor array technology has been intensively investigated in recent years (Persaud and Pelosi, 1985; Abe et al., 1987; Shurmer et al., 1990; Gardner and Bartlett, 1994; Hatfield et al., 1994; Tan et al., 1995; Hodgins, 1995; Nitz et al., 1999).

It has been hoped that instruments realized by means of this technology, commonly known as “electronic noses”, would provide an alternative to classical analytics.

Basically, these instruments comprise a set of non-selective but different sensor elements housed in a sensor chamber. Upon introducing analytes into the system, the sensor elements provide a signal pattern characteristic of the mixtures of volatiles present. This signal pattern is then evaluated using multivariate statistics such as pattern recognition techniques. There

are three well-known types of chemosensors used in these instruments: inorganic metal oxide semiconductors, conducting organic polymers, and mass sensitive piezoelectric sensors coated with GC stationary phases.

Just recently, the field of “electronic nose” technology has been extended by introducing mass spectrometry as a sensing principle (Nitz et al., 1998; Dittmann et al., 1998). In mass spectrometry based chemosensors, volatile sample components are introduced into the mass spectrometer without separation and a mass spectrometric pattern characteristic of the unseparated mixture of volatiles is created. Each measured fragment ion represents a potential sensing element, and the intensity of the fragment ion is equivalent to the sensor signal.

As in common chemosensors, this signal pattern is treated with pattern recognition methods.

Opposite to common chemosensors, the size and type of the sensor array can be changed rapidly by changing the fragment ions used for data evaluation. Moreover, the sensitivity of the instruments can be enhanced by variation of the scanning parameters from full scan technique to the selected ion monitoring mode.

It is this adaptable selectivity and sensitivity that makes this “new sensor technology” a potent tool for quality assessment and quality control purposes: The sensor array can be tailored toward every single application so that discriminations and classifications on the basis of desired sample properties can be achieved. In return however, their performance is crucially dependent on the method used when performing measurements. To obtain reliable classification results, a suitable measurement method has to be developed thoroughly before performing MS-sensor measurements.

It was the one objective of this study to develop a sensor-MS method to control the dosage of garlic flavoring in tomato sauces. A second objective was to evaluate whether this method was suitable to differentiate between tomato sauce flavored with different types of garlic flavoring.

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**Table 1. Headspace Composition (Percent Total Ion Current) of Selected Samples as Obtained with SPME-GC/MS**

peak no.	compd	RI <sup>a</sup>	% composition				
			A	B3	C3	D3	E
1	carbon dioxide, hexane <sup>c</sup>	786	n.d. <sup>b</sup>	n.d. <sup>b</sup>	n.d. <sup>b</sup>	n.d. <sup>b</sup>	n.d. <sup>b</sup>
2	dimethyl sulfide	837	29.45	0.57	1.44	2.59	10.11
3	diallyl sulfide	1162		25.03	1.49	13.13	22.84
4	limonene	1209	27.86	4.28	1.46	1.11	7.51
5	methyl allyl disulfide	1288		3.08	9.83	4.16	
6	6-methylhepten-2-on	1345	39.59	10.37	4.69	1.43	8.55
7	diallyl disulfide	1482		45.65	78.28	72.62	48.67
8	C <sub>6</sub> H <sub>10</sub> S <sub>2</sub>	1487		n.r. <sup>d</sup>	n.r. <sup>d</sup>	0.6	n.r. <sup>d</sup>
9	1,2-dithiocyclopentene	1523		9.00	2.19	3.50	2.31
10	geranial.	1730	3.10				
11	3-vinyl-4H-1,2-dithiin			2.02	0.62	0.89	
total peak area [10 <sup>8</sup> ion counts]			3.95	27.65	70.36	70.80	13.26

<sup>a</sup> Linear retention index on DBWax column. <sup>b</sup> Not determined. <sup>c</sup> Trace. <sup>d</sup> Not resolved.

## EXPERIMENTAL PROCEDURES

**Materials.** Four different commercially available garlic flavorings were added to a tomato base sauce prepared from tomato powder, water, salt, and sunflower oil. Sample properties of the samples included in this study were as follows:

(A) Blank tomato sauce. No flavoring was added to the tomato sauce.

(B) Flavoring type "roasted garlic", essential oil. Flavoring was added giving concentrations (w/w or g flavoring/100 g tomato sauce) of 0.01% (B1), 0.03% (B2), and 0.09% (B3).

(C) Flavoring type "fried garlic", essential oil. Flavoring was added giving concentrations of 0.08% (C1), 0.25% (C2), 0.75% (C3).

(D) Flavoring type "fresh garlic", powder. Flavoring was added giving concentrations of 0.125% (D1), 0.375% (D2), and 1.11% (D3).

(E) Flavoring type "cooked garlic", powder. Flavoring was added giving a concentration of 3.0%.

After preparation, flavored tomato sauces were stored at -20 °C in 100 mL glass jars with screw cap lids.

**Sample Preparation.** For all analyses, 2 g of sample was placed in a 20 mL glass vial, which was then crimp-capped with a Teflon-lined septum.

**Headspace-Gas Chromatography–Mass Spectrometry (HS-GC/MS).** All HS-GC/MS analyses were performed on a Finnigan 4500 mass spectrometer (Bremen, Germany) coupled to a Siemens Sichromat 1-4 series gas chromatograph, equipped with a Perkin-Elmer HS40 (Überlingen, Germany) autosampler for static headspace sampling. The capillary column used was a DB5 fused silica capillary column (J&W, 30 m × 0.25 mm i.d., film thickness 1.5 μm).

Headspace conditions were as follows: thermostating for 5 min at 40 °C (shaking); time of injection 0.2 min; needle temperature 55 °C; temperature of transfer tube 140 °C.

Temperature programming for gas chromatographic analysis was 60 °C (5 min)–5 °C/min–200 °C (10 min). Linear retention indices for the volatile components were calculated with *n*-alkanes (C<sub>6</sub>–C<sub>16</sub>) as references.

**Full Scan.** Mass spectra were obtained by EI ionization at 70 eV over the range of 33–300 mass units, with an ion source temperature of 150 °C. The scanning rate was 1 scan/s. Compounds were identified by comparing their mass spectra with those contained in the NIST/EPA/NIH Mass Spectral Database.

**Selected Ion Monitoring.** Mass spectra were obtained by EI ionization at 70 eV in the selected ion mode. Fragment ions with mass-to-charge ratio *m/z* 73, 81, 114, and 120 were measured with a dwell time of 250 ms per ion, respectively. The ion source temperature was 150 °C.

**Solid-Phase Microextraction (SPME).** The fiber used was coated with a 100 μm layer of PDMS, length 10 mm. For each SPME analysis, 2 g of sample was placed in a 20 mL glass vial, which was then crimp-capped with a Teflon-lined septum. The stainless steel needle, housing the fiber, penetrated the septum. Then the fiber was pushed out of the needle

and exposed to the headspace above the sample for 60 min at room temperature (20 °C).

SPME-GC/MS analyses were performed on a Finnigan 4500 mass spectrometer coupled to a Finnigan 9600 series gas chromatograph. The capillary column used was a DB Wax fused silica capillary column (J&W, 60 m × 0.25 mm i.d., film thickness 0.25 μm).

The SPME fiber was desorbed for 2 min in the GC split/splitless injection port, which was held at 220 °C. The injection port was in splitless mode, the splitter opening after 3 min. The oven was held at 60 °C during desorption.

After desorption, the GC oven temperature was held at 60 °C for 8 min, then increased to 170 °C at 2 °C/min (no hold), and finally increased to 200 °C at 6 °C/min (90 min hold). Helium was used as carrier gas with a flow of 1.26 mL/min at 100 °C. A split ratio of 11:1 (100 °C) was used. The mass spectrometer operated in EI mode with an electron energy of 70 eV, the scanning range used was 33–400 amu with a scanning rate of 1 scan/s. The temperature of the ion source was 150 °C.

**MS-Sensor Analysis.** All analyses were carried out on a Perkin-Elmer MS-Sensor (Norwalk, CT).

Conditions for static headspace sampling were kept identical to those used in the HS-GC/MS analyses with one exception: For MS-Sensor analyses, injection time was 2 min.

Mass spectra were obtained by EI ionization at 70 eV in the selected ion mode. Fragment ions with mass-to-charge ratio *m/z* 73, 81, 114, and 120 were measured with a dwell time of 250 ms per ion, respectively. The ion source temperature was 150 °C, a split ratio of 1:4 was used.

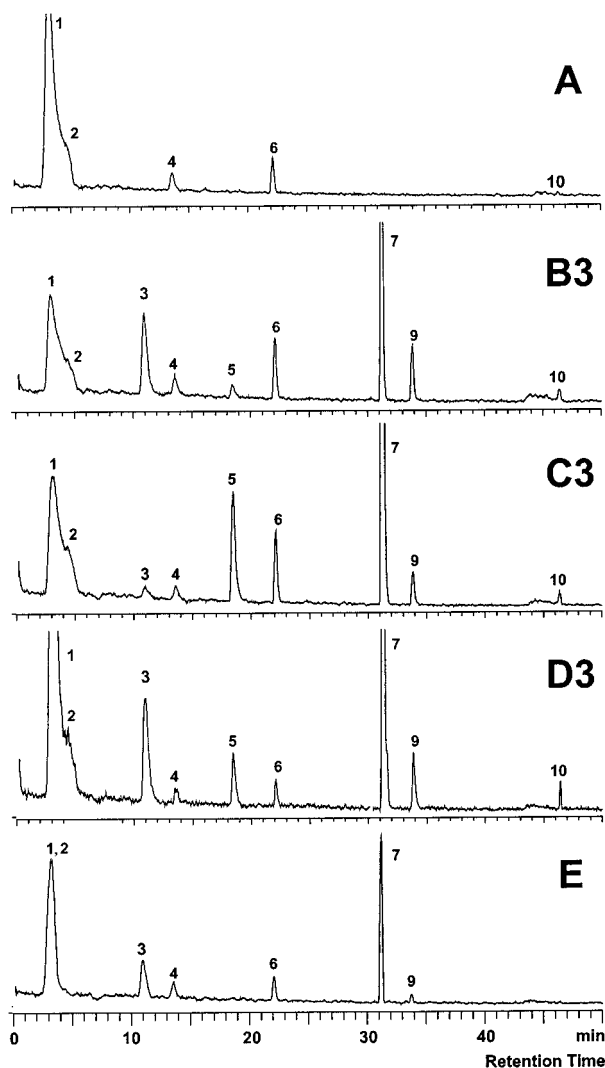
The multivariate data (four-dimensional) were evaluated by principal component analysis for visualization and multivariate discriminant analysis for classification, using the QMBSOFT NT software (HKR Sensorsysteme GmbH, Munich).

A set of 10 measurements was collected for each sample class.

## RESULTS AND DISCUSSION

**SPME-GC/MS Analysis.** SPME analysis was used to determine the headspace composition of tomato sauces blended with four garlic flavorings. Typical GC/MS chromatograms of the volatiles present in the headspace above samples B3, C3, D3, and E, containing the highest amount of each flavoring, are shown in Figure 1. Table 1 shows the percentage composition of the headspace for these samples. A total of 11 volatile compounds were identified.

As can be seen, diallyl disulfide, diallyl sulfide, and methyl allyl sulfide were the major volatile components present in the headspace above flavored tomato sauce samples. They, as well as the minor compounds methyl allyl disulfide, 1,2-dithiocyclopentene, and 3-vinyl-4H-1,2-dithiin found in some samples, are known to be



**Figure 1.** Total ion chromatograms of volatiles obtained from garlic-flavored (B3, "roasted"; C3, "fried"; D3, "fresh"; E, "cooked") and unflavored (A) tomato sauce. Peak numbers listed correspond with those listed in Table 1.

present in garlic essential oils (Jirovetz et al., 1992; Yu et al., 1989; Kim et al., 1995a), aqueous and solvent extracts of fresh garlic bulbs (Mazza et al., 1992), and garlic products prepared by different methods (Yu et al., 1993; Kim et al., 1995b). They are known to contribute to the flavor of garlic products. Whereas diallyl sulfide evokes a pungent, horseradish-like note, diallyl disulfide is known to add a savory, onion-like sensation.

They are transformation products of alk(en)yl thiosulfinates (Block et al., 1986; Iberl et al., 1990a; Lawson et al., 1991; Lawson, 1992; Block, 1992), the primary flavor compounds in raw garlic (Stoll and Seebeck, 1951): When thermally treated at temperatures above 150 °C, alk(en)ylthiosulfinates decompose and rearrange to disulfides (Brodnitz et al., 1971) and vinyldithiins such as 2-vinyl-4*H*-1,3-dithiin and 3-vinyl-4*H*-2,2-dithiin (Block, 1985; Yu and Wu, 1989). These rearrangement are known to take place not only during processing of garlic products such as frying or baking, but also upon gas chromatography with high injector port temperatures (Block, 1985).

Finally, it has been reported that diallyl sulfide and diallyl disulfide are formed by decomposition and rearrangement of (very unstable) diallyl thiosulfinate

**Table 2.** Abundances of Fragment Ions  $m/z$  73, 81, 114, and 120 in the Mass Spectra of Selected Volatiles

	$m/z$ 73	$m/z$ 81	$m/z$ 114	$m/z$ 120
diallyl sulfide	71.87	17.92	40.24	
methyl allyl disulfide	59.80	2.80		100.00
diallyl disulfide	8.91	26.12	0.50	

(allicin) in fresh garlic even at room temperature (Brodnitz et al., 1971).

As a consequence, due to different preparation methods, various types of garlic flavorings differ in the concentrations of sulfide compounds and vinyldithiins. It should therefore as well be possible to discriminate samples of tomato sauce blended with different types of garlic flavorings, with the discrimination based on the differences in the headspace concentrations of sulfides and vinyldithiins.

As for the volatiles released from the garlic flavoring, SPME-GC/MS analysis indicated that concentrations of diallyl disulfide and methyl allyl disulfide were highest in the headspace above samples containing "fried"-type (C3) and "fresh"-type (D3) flavoring, whereas diallyl sulfide was most abundant in samples blended with "fresh"-type (D3) and "roasted"-type (B3) flavoring. 3-Vinyl-4*H*-1,2-dithiin could be found in all flavored samples except those blended with "cooked"-type flavoring. 1,2-Dithiocyclopentene was present in all flavored samples. Due to the rather low absolute gas-phase concentration of diallyl disulfide in the headspace of the "roasted"-type, 1,2-dithiocyclopentene accounts for 9% of the total headspace in samples with "roasted"-type flavoring, although its (absolute) concentration in the gaseous phase is comparable to the "fresh"-type and "fried"-type samples.

Volatiles released by the pureed tomato fruit were dimethyl sulfide, limonene, 6-methyl-hepten-2-one, and geranial. They have been described previously to be present in fresh and processed tomato fruit: Dimethyl sulfide is the major volatile component of tomato puree (Belitz and Grosch, 1992a). With a low odor threshold of 1.0  $\mu\text{g/L}$  in water (Belitz and Grosch, 1992b), dimethyl sulfide is one of the most important flavor compounds in processed tomato products. 6-Methyl-hepten-2-one, limonene, and geranial are volatile constituents of fresh tomato fruits (Petro-Turza, 1987; Buttery et al., 1987; Buttery et al., 1988; Buttery et al., 1989).

For MS-sensor measurements, fragment ions with mass-to-charge ratio  $m/z$  73, 81, 114, and 120 were chosen as "sensor array". These fragment ions are present in the mass spectra of diallyl sulfide, methylallyl disulfide, and diallyl disulfide; their relative intensities in these spectra are shown in Table 2. As the concentration of diallyl sulfide, methylallyl disulfide, and diallyl disulfide can be considered characteristic for both flavoring type and concentration, the intensities of  $m/z$  73, 81, 114, and 120 recorded in a HS-MS measurement should be likewise characteristic for the investigated flavored samples.

**HS-GC/MS (Full Scan) Analysis.** HS-GC/MS studies in the full scan mode were carried out to record the headspace composition when static headspace sampling is used for sample delivery. They were aimed to evaluate whether, in full scan mode, intensities of  $m/z$  73, 81, 114, and 120 were sufficient to tell apart tomato sauce samples blended with different flavor types and concentrations.

In all samples, dimethyl sulfide was the major component accounting for 85% (D3)–100% (A, B1, C1, D1)

**Table 3. HS-GC/MS (SIM) Analysis. Peak Areas of Fragment Ions  $m/z$  73, 81, 114, and 120**

		A	B1	B2	B3	C1	C2	C3	D1	D2	D3	E
$m/z$ 73	n.i. <sup>a</sup> (RI <sup>b</sup> 610)											2.65
	n.i. <sup>a</sup> (RI <sup>b</sup> 704)		1.57	2.63	24.77			1.30	2.15	5.57	19.14	20.42
	diallyl sulfide		2.96	3.94	16.50		0.29	1.97	2.41	9.09	33.2	11.64
	methyl allyl disulfide						0.48	1.93		0.46	1.13	
	diallyl disulfide						0.44	2.80		0.83	3.34	0.25
	<b>sum</b>		<b>4.53</b>	<b>6.57</b>	<b>41.27</b>		<b>1.21</b>	<b>8.0</b>	<b>4.56</b>	<b>15.95</b>	<b>56.81</b>	<b>34.96</b>
$m/z$ 81	n.i. <sup>a</sup> (RI <sup>b</sup> 610)		0.98	1.67	3.80	0.20	0.56	0.53	0.45	0.63	1.19	1.66
	n.i. <sup>a</sup> (RI <sup>b</sup> 704)							0.21			0.14	
	diallyl sulfide		0.56	0.94	2.16			0.54	0.62	2.14	8.30	3.17
	methyl allyl disulfide							0.27				
	limonene	0.18	0.21	0.18	0.20	0.08	0.20	0.07	0.13	0.15	0.23	0.25
	diallyl disulfide				0.36	0.19	0.50	3.57	0.34	1.03	4.46	0.45
	<b>sum</b>	<b>0.18</b>	<b>1.75</b>	<b>2.86</b>	<b>6.52</b>	<b>0.47</b>	<b>1.26</b>	<b>5.19</b>	<b>1.54</b>	<b>3.95</b>	<b>14.32</b>	<b>5.53</b>
$m/z$ 114	diallyl sulfide		1.05	1.11	4.04			0.45	0.82	2.38	9.43	3.42
	diallyl disulfide							0.48		0.12	0.51	
	<b>sum</b>		<b>1.05</b>	<b>1.11</b>	<b>4.04</b>			<b>0.93</b>	<b>0.82</b>	<b>2.50</b>	<b>9.94</b>	<b>3.42</b>
$m/z$ 120	methyl allyl disulfide			0.14	1.14	0.32	1.45	8.07	0.43	1.34	4.72	0.49
	<b>sum</b>			<b>0.14</b>	<b>1.14</b>	<b>0.32</b>	<b>1.45</b>	<b>8.07</b>	<b>0.43</b>	<b>1.34</b>	<b>4.72</b>	<b>0.49</b>

<sup>a</sup> Not identified. <sup>b</sup> Linear retention index on DB5 column.

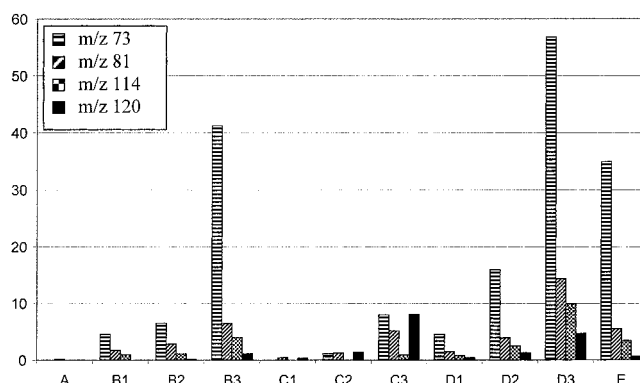
of the total peak area. Volatiles released from the garlic flavoring could only be detected in those three samples that, by SPME-GC/MS, were found to have the highest overall concentrations of volatiles in the headspace: D3, B3, and C3. In these samples, diallyl sulfide and diallyl disulfide were present in concentrations that resulted in complete (full scan) spectra. The concentration of diallyl sulfide and diallyl disulfide in the headspace above samples B2, C2, and D2 resulted in incomplete spectra, their concentrations in samples of lowest flavoring concentration B1, C1, and D1 did not exceed the detection limit of HS-GC/MS (full scan) at all. Therefore, the full scan mode was considered unsuitable for MS-sensor measurements.

Besides, HS-GC/MS measurements indicated that the concentration of DMS was D3 > A > B3 > E > C3, whereas SPME analysis indicated a concentration gradient of D3 > E > A > C3 > B3. As DMS is very volatile, the differences in results seem to be caused by evaporation of DMS during sample preparation (opening time of jars; time span until headspace vials are filled and closed) and storage.

**HS-GC/MS (Selected Ion Monitoring) Analysis.** The results of the HS-GC/MS analyses carried out in the selected ion monitoring mode with  $m/z$  73, 81, 114, and 120 are shown in Table 3.

For all types of flavored samples, the intensities of the measured fragment ions increase with higher flavoring dosages. As flavoring dosages differ by a factor of 3 for every type of flavor, one might expect the respective peak areas to multiply by a factor of 3, too. However, this is not the case. Differences in peak area range from a factor of 1.44 for  $m/z$  73 in samples B1–B2 to a factor of 15 for  $m/z$  73 in samples B2–B3. Differences in peak area are most striking for samples where essential oil flavoring has been added to the sauce. In samples with powdered flavoring—D1, D2, and D3—peak areas differ by a factor of 2.6 ( $m/z$  81 in samples D2–D3) to 4 ( $m/z$  114 in samples D2–D3). It cannot be excluded that loss of volatiles occurs during storage of the “stock solutions” and filling of the headspace vials before analysis.

Besides diallyl sulfide, methylallyl disulfide, and diallyl disulfide, two unknown substances with retention indices RI 610 and 704 (on DB5 column) undergo fragmentation to give  $m/z$  73 and 81. These substances seem to be present in flavored samples only, but could not be identified in this study. In addition,  $m/z$  81 is

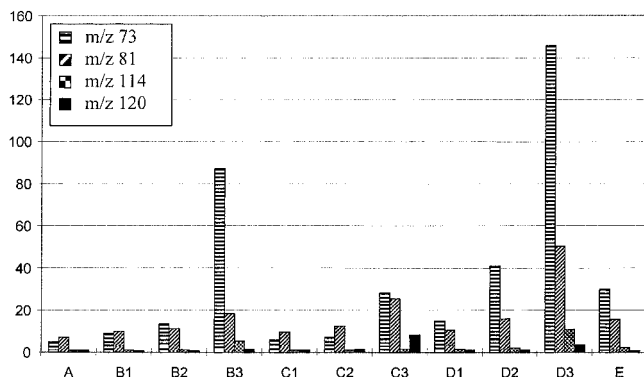
**Figure 2.** HS-GC/MS (SIM) analysis. Summed peak areas for  $m/z$  73, 81, 114, and 120 [ $10^5$  ion counts].**Table 4. HS-MS Analysis. Intensities of Fragment Ions  $m/z$  73, 81, 114, and 120 [ $10^4$  Ion Counts]**

	$m/z$ 73	$m/z$ 81	$m/z$ 114	$m/z$ 120
A	4.88	7.05	0.99	0.86
B1	8.89	9.86	1.06	0.73
B2	13.44	11.22	1.18	0.70
B3	87.28	18.40	5.40	1.39
C1	5.94	9.65	0.98	1.07
C2	7.16	12.42	1.02	1.34
C3	28.24	25.39	1.50	8.15
D1	14.88	10.39	1.32	0.96
D2	40.78	15.83	2.08	1.15
D3	145.84	50.26	10.88	3.47
E	30.06	15.55	2.18	0.78

present in the spectra of limonene, a substance released from the tomato sauce. As concentrations of limonene in all samples are rather similar, pattern recognition will not be affected by its contribution to the intensity of  $m/z$  81 in HS-MS measurements.

Diallyl sulfide and diallyl disulfide account for 100% of the peak area sum of  $m/z$  114, as does methylallyl disulfide for  $m/z$  120, respectively.

**HS-MS Analysis.** Table 4 lists the mean intensities of  $m/z$  73, 81, 114, and 120 obtained by sensor-MS analyses for the investigated samples. Figure 3 shows their signal patterns, respectively. As expected, intensities of fragment ions increase with flavoring concentration in the respective samples. Highest overall intensities of fragment ions  $m/z$  73 and 81 were recorded for samples D3; not surprisingly, as these samples were found to contain the highest amounts of diallyl sulfide and diallyl disulfide in SPME analysis.



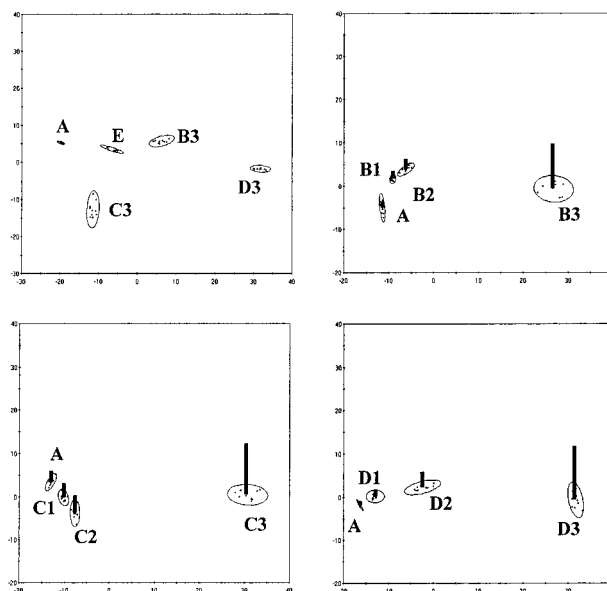
**Figure 3.** HS-MS analysis. Array response pattern for fragment ions  $m/z$  73, 81, 114, and 120 [ $10^4$  ion counts].

**Table 5.** HS-GC/MS (SIM) Analysis. Summed Peak Area of Fragment Ions  $m/z$  73, 81, 114, and 120 [ $10^5$  Ion Counts]

	$m/z$ 73	$m/z$ 81	$m/z$ 114	$m/z$ 120
A		0.18		
B1	4.54	1.75	1.05	
B2	6.57	2.86	1.11	0.14
B3	41.27	6.52	4.04	1.14
C1		0.47		0.35
C2	1.21	1.27		1.45
C3	8.00	5.19	0.93	8.07
D1	4.56	1.54	0.82	0.43
D2	15.95	3.95	2.50	1.34
D3	56.81	14.33	9.94	4.72
E	34.98	5.53	3.42	0.64

In general, intensities of fragment ions measured when directly injecting the headspace into the MS show good correlation with the summed peak areas calculated on the basis of the HS-GC/MS (SIM) analysis (Table 5). As can be seen in Figures 2 and 3, signal patterns obtained with HS-MS are very similar to patterns of summed peak areas resulting from HS-GC/MS (SIM).

**Pattern Recognition.** Eleven classes were formed by combining the HS-MS data of 10 measurements of samples with same properties (type and concentration of flavoring added). Principal component analysis was applied to these HS-MS data. The aim of this analysis was to separate different classes. The result of the analysis is visualized graphically by a discrimination plane (Figures 4a–d), with each plane being made of the first and second principal component. Principal component analysis resulted in good separation of all these classes. As shown in Figure 4a, the classes that represent those tomato sauces with highest concentrations of flavorings (B3, C3, D3, E) form exclusive ellipses on the discriminant plane. These ellipses are both clearly separated from each other and the ellipse that represents the blank tomato sauce. Hence, it is possible to use the MS-sensor to differentiate between tomato sauces with different flavorings. Moreover, the dosage of flavoring can be followed as well. As shown in Figure 4b–d, classes of tomato sauce samples with different concentrations of flavoring are clearly separated. In all cases, classes of samples with lower concentration of flavoring are located near classes of samples of the blank tomato sauce. Classes of samples with higher flavor concentrations are more distant of classes of unflavored samples. It can be observed that, for a particular flavoring, all samples (and classes) are located in a rather straight ribbon which directed to the first principal component. This can best be observed for samples blended with “fresh garlic” flavoring D (Figure 4d). This



**Figure 4.** Graphic feature space (a) different types of garlic flavoring; (b) garlic flavoring type “roasted”, different concentrations; (c) garlic flavoring type “fried”, different concentrations; (d) garlic flavoring type “fresh”, different concentrations. Bars are a measure for mean ion intensity.

confirms that differences in flavor concentrations are responsible for the separation of the classes.

## CONCLUSION

The principle objective of this study was to evaluate the use of the MS-sensor in dosage control of garlic flavorings. For this purpose, a method has been developed that was suitable for monitoring the concentration of the flavoring and discriminating between different types of garlic flavoring added to tomato sauce. Based on the information about volatile sample constituents obtained in SPME-GC/MS analysis and HS-GC/MS (full scan) analysis, a set of four fragment ions was chosen as sensor array:  $m/z$  73, 81, 114, and 120 are present in diallyl sulfide, methylallyl disulfide and diallyl disulfide—volatiles characteristic for raw and processed garlic products. HS-MS measurements were backed by HS-GC/MS (SIM) measurements.

Results indicate that the MS-sensor can be implemented as a quality control device in the area of seasoning dosage. With proper method development, this instrument works well in determining the relative differences in headspace compositions of different flavorings. As the measurement procedure is much faster, cheaper, and easier than common GC/MS determinations, this instrument might become a challenging promise for the food industry.

## ABBREVIATIONS USED

FID, flame ionization detector; GC, gas chromatography; HS, headspace; MS, mass spectrometry; SPME, solid-phase microextraction.

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