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Evaluation of three gas chromatography and two direct mass spectrometry techniques for aroma analysis of dried red bell peppers

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Abstract

Three gas chromatography methods and two direct mass spectrometry techniques were compared for the analysis of the aroma of rehydrated diced red bell peppers. Gas chromatography methods included systems with olfactometry detection (GC–O), flame ionisation detection (GC–FID) and mass spectrometry (GC–MS). The evaluated direct mass spectrometry techniques involved atmospheric pressure chemical ionisation–time-of-flight mass spectrometry (APCI–TOFMS) and proton transfer reaction–mass spectrometry (PTR–MS). The relevance of the aroma component of the flavour was shown by sensory analysis. High intensity scores were obtained for the aroma attributes 'bell pepper,' 'cooked vegetables' and 'grassy.' Sixty-three volatile compounds were identified in the headspace of the bell peppers by GC–MS. According to GC–O analysis, 11 compounds possessed odour activity. Consistently across all techniques, 3-methylbutanal was the most abundant odour active compound, followed by 2-methylbutanal. Compounds present at low concentrations were more affected by the methodology. Chromatography methods correlated strongly with each other ($\rho = 0.946$), whereas the direct mass spectrometry methods showed less significant correlation ($\rho = 0.613$). Examining differences across all methods, it appeared that the proportions of the odour active compounds were not significantly different for GC–MS, GC–FID and PTR–MS. Significant differences were observed for APCI–TOFMS and the other techniques ($P < 0.01$). (Int J Mass Spectrom 223–224 (2003) 55–65)

Keywords: APCI–TOFMS; GC–FID; GC–MS; GC–O; PTR–MS

1. Introduction

The chemical composition of foods is highly complex and comprises both volatile and non-volatile substances. Some of these substances contribute to the flavour of foods. Since the aroma component (volatile flavour) is usually responsible for the characteristic flavour of foods, the volatile compounds have received most attention [1]. In the early stages of aroma research, most emphasis has been on development of methods to establish the chemical identity of the aroma constituents. The analytical task is rather

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complicated, as the fraction of aroma compounds of a simple food may be composed of 50–200 constituents, and these compounds are present in trace quantities. The large number of aroma chemicals complicates the task even further. Aroma science has benefited from the progress in the analysis techniques over the last decades, which led to long lists of volatiles (>6000) determined in foods [2]. Initially, the total volatile composition of a food was measured, for which extraction and distillation methods were employed, in combination with gas chromatography (GC). Later it appeared that the concentration of volatile compounds in a food does not necessarily reflect their concentration in air, as the concentration in air not only depends on the concentration in the food product but also on the interactions between the food matrix and the volatiles. The sensory perception of aroma is determined by the concentration of volatile compounds in the air phase. Therefore, headspace concentrations usually relate better to sensory properties than concentrations in the food product. Analysis methods, therefore, shifted from analysis of the compounds in the food to analysis of the volatile compounds in the air around the food (the headspace). Static and dynamic headspace measurements have become extensively used. This type of analysis developed further with the use of in-mouth analogues and in-mouth and in-nose measurements [3,4].

Indications that only a small fraction of the large number of volatiles occurring in food actually contributes to the aroma [5], led to an interesting technique: gas chromatography–olfactometry (GC–O). The technique involves the sniffing of the gas chromatographic effluent by assessors in order to associate odour activity with eluting compounds, sometimes with a part of the effluent split to an instrumental detector. It is well known that many detectors are not as sensitive as the human nose for odour active compounds [6].

The last 5 years have seen research groups developing methods to measure the change of the aroma profiles of foods during the time course of eating. Collection of air at the nostril(s) of subjects is the usual practice [7]. Initially, these time–intensity measurements were conducted by trapping volatile compounds for short time intervals (e.g., 15 s). Absorbents and cryo-trapping have been used successfully in combination with GC–mass spectrometry (GC–MS).

Direct inlet mass spectrometry has been developed more recently, and led to improved resolution of the measurements from ca. 15 to 0.2 s. Taylor and coworkers developed an interface for the detection of volatiles in expired air from people during consumption of food [8]. They applied atmospheric pressure chemical ionisation–mass spectrometry (APCI–MS) for headspace analysis as well as for in-nose and in-mouth aroma analysis. APCI–MS is a ‘soft’ ionisation method that causes little fragmentation of the compounds and produces mainly molecular ions by addition or abstraction of a proton. Most molecules (R) are ionised by addition of a proton in positive ionisation mode to give $R + H^+$ [1].

Another direct mass spectrometry technique, proton transfer reaction–mass spectrometry (PTR–MS), was developed by Lindinger et al. and was introduced in 1993 [9]. What distinguishes PTR–MS from APCI–MS is that the generation of the primary H_3O^+ and the chemical ionisation of the volatile compounds are individually controlled and spatially and temporally separated processes. One important consequence is that absolute headspace concentrations can be calculated without calibration or addition of standards [10]. Although PTR–MS has not been as commonly used as APCI–MS, environmental applications [11] and medical applications have been published [12]. Additionally, PTR–MS has shown to be useful for flavour analysis [13–16].

Valuable aroma data have been generated with the various methods, with some systems being used more than others. A direct comparison of the conventional gas chromatographic techniques and the more recently developed direct mass spectrometry techniques would demonstrate how these data relate to each other. In the present study, GC–O, GC–flame ionisation detection (GC–FID) and GC–MS are compared with APCI–time-of-flight MS (APCI–TOFMS) and PTR–MS for analysis of the aroma of dried diced red bell peppers. Sensory analysis was conducted on the bell peppers to determine the contribution of the aroma to the overall flavour.

2. Experimental

2.1. Materials

Commercially dried diced red bell peppers from Turkey were supplied by Top Foods b.v. (Elburg, The Netherlands). The bell peppers were stored in glass jars at 4 °C in absence of light. For rehydration, bell peppers were placed in a glass flask and water was added (ratio 1.2:10 w/w). The bell peppers were boiled for 10 min.

2.2. GC–O, GC–FID and GC–MS analyses

Dynamic headspace analyses were carried out on the rehydrated diced bell peppers using GC–O, GC–FID and GC–MS. Experimental conditions of the isolation of the volatiles from the bell peppers, conditions during the thermal desorption and during the GC analyses were identical for the three analysis methods throughout the experiments and have been reported previously [17]. For GC–O analysis, the GC effluent was split 30:35:35 for FID, sniff port 1 and sniff port 2, respectively. Twelve assessors were selected and trained for GC–O analysis. The assessors generated odour descriptors during preliminary sessions on the aroma of dried bell peppers of various origins. The descriptors were clustered after focus groups resulting in a list of 20 descriptors (bell pepper, burned/rubber, cooked vegetables, fresh vegetables, fruity, grassy/green, mushrooms, sour, spicy, sweet, butter, caramel, chocolate, coffee, fish, lemon-/orange-like, onion/leek, plastic/chemical, rotten, sickly). One of the descriptors or ‘other/I do not know’ had to be selected for each compound detected by an assessor during the analysis. Blank Tenax traps without absorbed volatiles were used to determine the noise level. The bell pepper sample was analysed in six sessions with two assessors sniffing simultaneously. The intensities of the aroma compound were expressed as the number of assessors perceiving an odour: the detection frequency. FID response was recorded simultaneously during the GC–O analysis resulting in six replicate measurements. Average FID peak areas (V s) were calculated. Two replicate GC–MS analyses were carried out. GC–MS analysis was used to identify the aroma compounds detected in GC–O and GC–FID analysis. Apart from identification, GC–MS resulted in semi-quantitative data of all volatile compounds, which were expressed as total ion counts (TIC).

2.2.1. APCI–TOFMS analysis

For APCI–TOFMS analysis a micromass volatile gas analyser (MS-NOSE, Micromass UK Ltd., Manchester, UK) was used, which consisted of a modified APCI source interfaced with a micromass orthogonal time-of-flight–mass spectrometer. The inlet system of the instrument consisted of a heated transfer line of fused silica tube (0.9 m length, 0.12 mm i.d., 150 °C) through which the headspace of the cooked bell peppers (1.2 g dry weight, placed in a 100 mL glass flask) was drawn at 70 mL min^{-1} in the source region (temperature 120 °C) by means of a Venturi effect produced by a variable counter flow of nitrogen gas (8.3 L min^{-1}). The exit region of the transfer line consisted of a reduced volume APCI source containing a corona discharge pin (3000 V/15.5 μA) where the analyte molecules were ionised and an extraction cone (18 V) which drew the ions produced, orthogonally, into the transfer region of the mass spectrometer. Ions produced in the source were transferred by ion optics to a pusher region operating at a cycle time of 20 kHz. The ions from each pusher cycle were spatially separated in the flight tube region, which consisted of a reflectron and multichannel plate (MCP) detector. The MCP was linked to a time to digital converter operating at 3.6 GHz, which recorded the ion arrival times at the MCP. These times were then converted to mass to charge (m/z) values with a resolution of 6000 (FWHM definition). The output from the individual pusher cycles were combined in an embedded computer to form an average (histogrammed) spectrum, over the full mass range, recorded, at a rate of 1 spectrum s^{-1}. The headspace was flushed to account for the dead volume of the system. The measurement was repeated twice. It was shown that the odour active compounds of the dried vegetables were linearly released between 1 and 12 min of isolation [18].

2.2.2. PTR–MS analysis

The rehydrated diced bell peppers were analysed by PTR–MS according to the method described by Lindinger et al. [19]. The diced bell peppers (1.2 g dry weight) were placed in a glass flask (300 mL). The headspace was drawn at 114 mL min^{-1} by a vacuum pump, 14 mL min^{-1} of which was led through a heated Teflon transfer line (1.0 m length, 1.6 mm i.d.) into the PTR–MS system for on-line analysis. For dynamic headspace analysis, the mass spectrometric data were collected for m/z 20–180 at a rate of 1 mass s^{-1}. The various measurements were replicated 10 times after an initial purge to account for the dead volume of the system.

Headspace concentrations of the compounds were calculated as described elsewhere [19] and were averaged. The majority of the proton transfer reactions were non-dissociative. For some compounds that showed dissociation during the proton transfer, standards provided information on the fragmentation pattern, and those findings were used for calculation of the headspace concentrations of the compounds.

2.2.3. Sensory analysis

A panel of 24 judges (aged 20–65) was selected and trained for analytical sensory analysis. Rehydrated diced red bell peppers (2.4 g dry weight) were served to the panel and perceived flavour intensities were scored on a 70 mm visual analogue scale. Flavour attributes were generated in preliminary sessions and clustered after focus groups, which resulted in a list of 14 attributes (bell pepper, burned, cooked vegetables, fresh, fruity, grassy, mushrooms, sour, spicy, sweet, bitter, cucumber, pungent, sharp). Average panel intensity scores were calculated for the various flavour attributes.

2.2.4. Statistical analysis

Spearman's ranked correlation coefficients were calculated from the data generated with the various techniques and their significance determined ($P < 0.05$ and $P < 0.01$).

3. Results and discussion

3.1. Sensory evaluation

An analytical sensory panel evaluated the rehydrated diced red bell peppers. Average intensity scores of the sensory attributes are presented in a spider-web diagram in Fig. 1. Although judges responded differently, the panel was consistent across replications. The peppers were characterised by 14 flavour attributes. Relatively high scores were obtained for the attributes 'bell pepper' (48), 'cooked vegetables' (48), 'grassy' (36), 'sweet' (36) and 'spicy' (30). Previous sensory studies on the dried vegetables showed that 'bell pepper,' 'cooked vegetables' and 'grassy' can be considered aroma attributes, whereas 'sweet' and 'spicy' contributed to both the aroma and taste component of flavour [17,20]. The drying process affects the flavour of vegetables considerably. van Ruth et al. [21] compared the flavours of three different vegetables after drying and the aroma of the bell peppers, French beans and leeks showed large similarities. In particular, the attributes 'cooked vegetables,' 'grassy,' 'mushroom,' 'spicy' and 'sweet' showed comparable intensities.

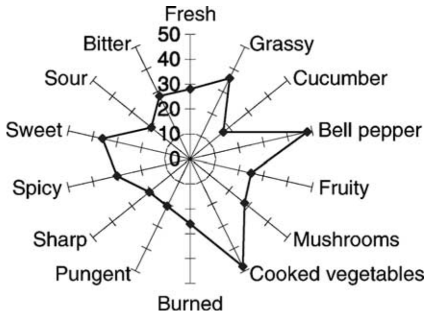

Fig. 1. Spider-web diagram of average intensity scores for sensory attributes of rehydrated diced red bell peppers ($n = 24$).

Table 1
Volatile compounds of dried bell peppers identified by gas chromatography–mass spectrometry and their TIC, $n = 2$

Compound	TIC	Compound	TIC	Compound	TIC
2-Methylpropanal	2080	1-Butanol	206	1-Octen-3-ol	604
Acetone	4095	1-Penten-3-ol	419	2-Isopentylthiophene	184
Methyl acetate	904	2-Heptanone	1055	Furfural	142
Tetrahydrofuran	1648	Heptanal	363	2-Nonen-4-one	1871
Butanal	446	2-Pentenal	80	2-Ethyl-1-hexanol	509
2-Methyl-2-propenal	580	2-Methyl-1-butanol	160	Decanal	1616
Ethyl acetate	4095	3-Methyl-1-butanol	325	Benzaldehyde	999
1,1-Diethoxy ethane	233	2-Hexenal	325	2-Methoxy-3-isobutylpyrazine	50
2-Butanone	3583	Octanal	479	2-Nonenal	227
2-Methylbutanal	4095	1-Octen-3-one	68	2-(2-Ethoxy)ethanol	800
3-Methylbutanal	6143	3-Hepten-2-one	1151	β-Cyclocitral	576
2-Propanol	3327	2,2,6-Trimethyl cyclohexanone	928	Safranal	540
3-Buten-2-one	319	1-Chlor-2-propanol (t[a])	1495	Acetophenone	384
Diacetyl	624	2-Heptenal	287	3-Methylbutyric acid	4095
Pentanal	3018	6-Methyl-5-hepten-2-one	815	α-Murolene	176
1-Penten-3-one	597	1-Hexanol	167	Ethyl benzaldehyde	392
2,3-Pentanedione	191	2-Nonen-4-one (t[a])	375	1-Phenylethanol	1736
Dimethylsulphide	90	Dimethyl trisulphide	880	Dimethylsulphone	1408
Hexanal	4035	Nonanal	616	2-Ethylhexanoic acid	248
3-Methylthiophene	165	3,3,5-Trimethyl-2-cyclohexanone (t[a])	468	Benzothiazole	251
2-Methyl-1-propanol	414	2-Octenal	436	Phenol	800

[a] t: tentative.

3.2. Dynamic headspace analysis: GC–MS

Dynamic headspace was conducted on the rehydrated diced red bell peppers. The volatile compounds were identified by GC–MS and further characterised by their retention indices and their odours described by the assessors in the GC–O analysis. The identified volatile compounds and their peak areas are presented in Table 1. Sixty-three compounds were identified and included alcohols, aldehydes, ketones, acids, esters and sulphur- and nitrogen-containing compounds. The five most abundant compounds were 3-methylbutanal, 2-methylbutanal, 3-methylbutyric acid, acetone and hexanal. Larger quantities of highly volatile compounds were found in comparison with other studies [22–24]. This difference is related to the extraction/distillation techniques used in other studies, which differs from the dynamic headspace method used presently. Extractions usually result in increased yields of higher molecular weight volatile compounds [25], and measure the concentrations of the compounds present in a food product. Dynamic headspace, on the other hand, measures the aroma concentrations in the gas phase and is more closely related to the conditions in the mouth.

3.3. Dynamic headspace analysis: GC–O and GC–FID

The volatile compounds of the bell peppers were subjected to combined GC–O/FID analysis. The identity of the odour active compounds was established by GC–MS, the data of which are presented in the previous section. GC–O of blank samples demonstrated that detection of an odour at the sniff port by 3 or less out of the 12 assessors can be considered as ‘noise.’ The odour descriptors generated in preliminary sessions for the odour active compounds of the bell peppers showed large similarity with the flavour attributes generated by the sensory panel (descriptors and attributes are stated in the Section 2). Table 2 presents the odour active compounds, descriptors, detection frequencies (numbers of assessors that perceived the compound) and the

Table 2
Odour active compounds of dried bell peppers determined by gas chromatography–olfactometry, their descriptors, detection frequency and average flame ionisation detection peak areas ($n = 6$)

Compound	Mass	Formula	Descriptor	Detection frequency	Peak area (V s)
2-Methylpropanal	72	C_4H_8O	Chocolate	9	12.0
2-Methylbutanal	86	$C_5H_{10}O$	Chocolate	12[a]	30.0
3-Methylbutanal	86	$C_5H_{10}O$	Chocolate		61.1
Diacetyl	86	$C_4H_6O_2$	Caramel, butter	9	0.3
1-Penten-3-one	84	C_5H_8O	Plastic, chemical	8	0.3
Hexanal	100	$C_6H_{12}O$	Grassy	12	15.7
Heptanal	114	$C_7H_{14}O$	Lemon/orange	5	1.5
Unknown	–	–	Fish, rotten	9	0.3
1-Octen-3-one	126	$C_8H_{14}O$	Mushroom	9	1.2
Dimethyl trisulphide	126	$C_2H_6S_3$	Rotten, onion/leek	11	0.5
2-Methoxy-3-isobutylpyrazine	166	$C_9H_{14}N_2O$	Bell pepper	12	0.1

[a] 2- and 3-methylbutanal could not be detected separately by the assessors.

FID peak areas. Eleven odour active compounds were detected: 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, diacetyl, 1-penten-3-one, hexanal, heptanal, 1-octen-3-one, dimethyl trisulphide, 2-methoxy-3-isobutylpyrazine and one other compound which could not be identified. The five compounds with the higher odour intensities were: 2-methoxy-3-isobutylpyrazine (bell pepper), hexanal (grassy), 2-/3-methylbutanal (chocolate) and dimethyl trisulphide (rotten, onion/leek). 2-Methoxy-3-isobutylpyrazine is the flavour character impact compound of bell peppers [22]. The presence of 2-methylbutanal, 3-methylbutanal and 1-octen-3-one is typical for dried vegetables [21,26]. The branched aldehydes are formed by Strecker degradation of (iso)leucine. Most other compounds are derived from lipid oxidation reactions [27]. That high abundance, reflected by large peak areas, does not necessarily coincide with high odour intensity is shown by the fact that the compounds with the largest peak area, i.e., 3-methylbutanal (61.1 V s), 2-methylbutanal (30.0 V s), hexanal (15.7 V s), and 2-methylpropanal (12.0 V s), did not match fully with the highly odour active compounds. Although 2-/3-methylbutanal and hexanal are present in relatively large quantities in the headspace and are relatively odour active, the other compounds show more variant results. An explanation is that dimethyl trisulphide has a very low threshold. Moreover, the FID is not very sensitive to sulphur compounds, nor to nitrogen-containing compounds like 2-methoxy-3-isobutylpyrazine.

3.4. Dynamic headspace analysis: APCI–TOFMS

The headspace of the bell peppers was analysed by APCI–TOFMS. A spectrum of the volatiles obtained by this high-resolution mass spectrometer is presented in Fig. 2. The most abundant masses measured were 87 (3955 TIC), 69 (3340 TIC), 73 (1096 TIC), 83 (499 TIC) and 151 (416 TIC).

Since the technique is unselective in its ionisation process, it is a one-dimensional technique and an unambiguous assignment of compounds requires additional sources of information [28]. In the present paper, the odour active compounds, previously selected by GC–O and identified by GC–MS were chosen to evaluate the analysis. From the spectrum in Fig. 2 it can be concluded that there are three abundant masses which correspond to the ionised masses of odour active compounds: mass 87 corresponds to the ionised mass of 2- and 3-methylbutanal and mass 73 to the ionised mass of 2-methylpropanal. The accurate mass measurements (four decimals) of the APCI–TOFMS allowed differentiation between compounds with the same nominal mass, but with different elemental compositions. The advanced software of the APCI–TOFMS calculated the formula of compounds matching the masses. Four of the

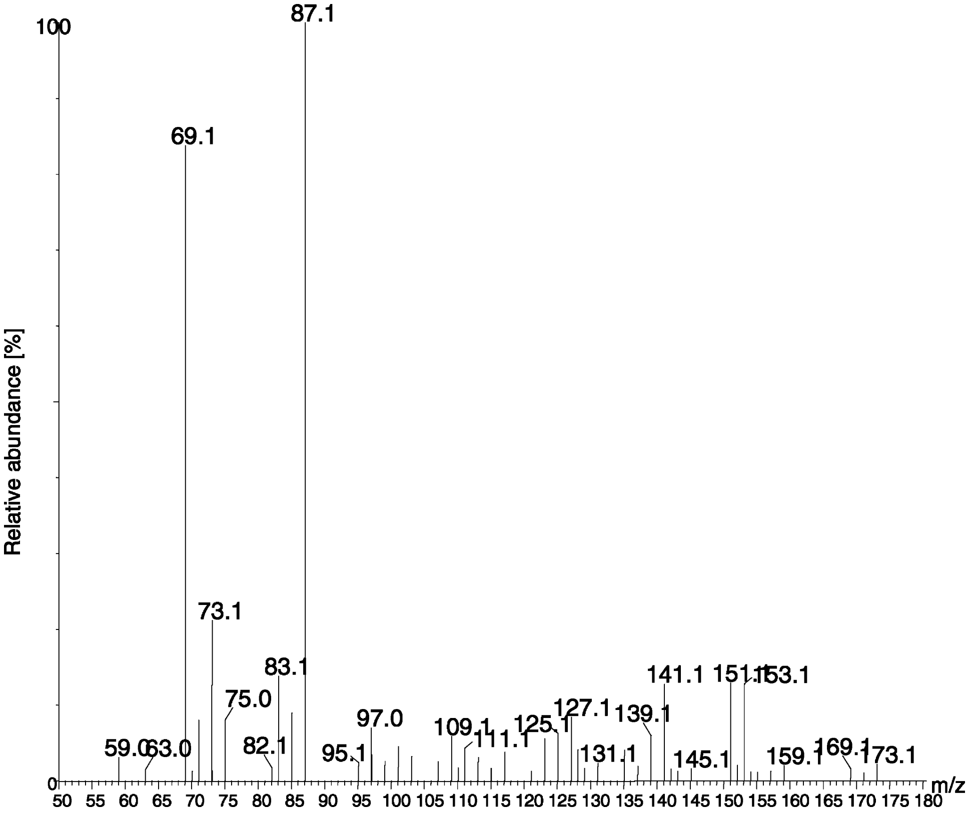

Fig. 2. Mass spectrum of the volatile compounds of rehydrated diced red bell peppers obtained by atmospheric pressure chemical ionisation–time-of-flight mass spectrometry.

formulas matched those of odour active compounds: 2-methylpropanal, 2-/3-methylbutanal, hexanal and heptanal (Table 3). Additionally, the TIC of the masses measured were identical to those of the odour active compounds presented in Table 3. Eight masses could be related to the 10 identified odour active compounds. The compounds that correspond to the five most abundant masses (high TICs) were in decreasing order: 2-/3-methylbutanal (3955), 2-methylpropanal (1096), 1-penten-3-one (296), 1-octen-3-one/dimethyl

Table 3

Measured ions corresponding to masses of odour active compounds of dried bell peppers, calculated formulas and relative headspace concentrations determined by atmospheric pressure chemical ionisation–mass spectrometry ($n = 2$)

Measured ion	Software calculated formula	Corresponding odour active compound	TIC
73.07	C_4H_9O	2-Methylpropanal	1096
85.07	–	1-Penten-3-one	296
87.08	$C_5H_{11}O$	2-/3-Methylbutanal	3955
101.09	$C_6H_{13}O$	Hexanal	164
115.01	$C_7H_{15}O$	Heptanal	60
127.12	–	1-Octen-3-one + dimethyl trisulphide[a]	295
167.12	–	2-Methoxy-3-isobutylpyrazine	48

[a] These isobaric compounds were not separated.

trisulphide (295). 2-Methylbutanal and 3-methylbutanal could not be differentiated due to their identical elemental composition. 1-Octen-3-one and dimethyl trisulphide were not found separately, which may be due to their isobaric characteristics or for detection threshold reasons. Particularly, dimethyl trisulphide is suspected with respect to detection limits because of its very low odour threshold.

The abundance of 2-/3-methylbutanal and 2-methylpropanal agreed with the GC–MS and GC–FID analyses. Hexanal was relatively low compared to data generated with the other techniques. Diacetyl required special attention, because it was not detected at all. The accurate mass measurement indicated that mass 87.0826 corresponded to the methylbutanals and not to diacetyl, although their nominal masses are identical. Fragmentation appeared not to be an issue. In order to investigate the cause for the missing diacetyl, the headspace of a mixture of 20 aroma compounds in sunflower oil (0.001% v/v, diacetyl air/oil partition coefficient 4.9×10^{-3} [29]) was analysed. The response to diacetyl was very low, and considerably diminished in comparison with other compounds, such as ethyl acetate, ethyl butyrate and 2-heptanone. A 1:10 dilution of the diacetyl and 19 other compounds in sunflower oil mixture showed a relative increase in response, although the response was still not proportional to the diacetyl headspace concentration as determined by calibrated GC–MS analysis. These results indicate suppression of the signal related to diacetyl. 2-Butanone showed a similar pattern at dilution. Compounds such as 1-propanol, ethyl acetate, 1-hexanol, ethyl butyrate and octanal did not show a change in relative response on dilution. Sunner et al. [30] suggested that ionisation in mixtures may be affected if one compound had a greater affinity for protons than another (selective suppression). Taylor et al. [1] reported concerns about selective ionisation of compounds, although they did not find any selective suppression for a mixture of seven aroma compounds. It has been suggested that non-quantitative measurements may also be related to the way the APCI source is operated [31]. In the present experiments, the conditions of the APCI source were optimised in the service laboratory of the manufacturer. However, the voltage of the APCI source was based on an overall response, as all ions were measured simultaneously. The voltage may not have been optimal for each of the individual compounds. In addition, it appears not impossible that selective suppression occurred which clouded the quantification aspect of the analysis.

3.5. Dynamic headspace analysis: PTR–MS

The dynamic headspace of the bell peppers was analysed by PTR–MS. A spectrum of the volatile compounds was obtained (Fig. 3). The masses measured in largest concentrations were 55 (198 nL L^{-1}), 59 (29 nL L^{-1}), 61 (15 nL L^{-1}), 73 (13 nL L^{-1}) and 69 (12 nL L^{-1}). Although most compounds were found as protonated masses, a few others showed fragmentation under the experimental conditions employed. For example, aldehydes and alcohols usually lost one molecule of water. Usually, it would be preferred to form one ion rather than two to optimise sensitivity. However, for isobaric compounds it may be worth to sacrifice some sensitivity to be able to discriminate the compounds on the basis of their different ion patterns. The fragmentation patterns of the odour active compounds were known and allowed quantification of the various compounds (Table 4). The experimental

Table 4
Odour active compounds and their average headspace concentrations determined by proton transfer reaction–mass spectrometry ($n = 10$)

Compound	Value (nL L^{-1})
2-Methylpropanal	20.0
2-Methylbutanal	71.6
3-Methylbutanal	84.2
Diacetyl	8.4
1-Penten-3-one	2.4
Hexanal	37.6
Heptanal	3.2
1-Octen-3-one + dimethyl trisulphide[a]	0.7
2-Methoxy-3-isobutylpyrazine	0.1

[a] These isobaric compounds were not separated.

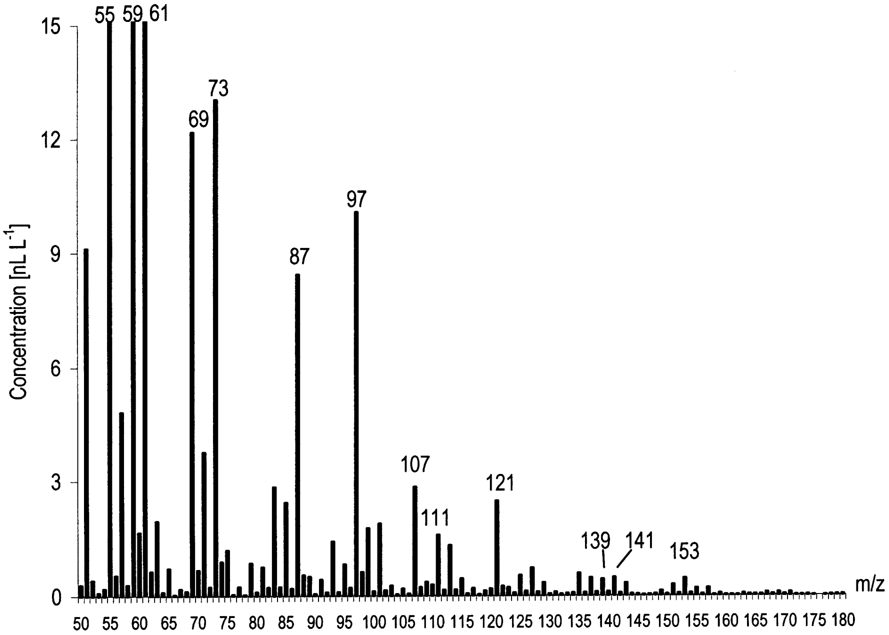

Fig. 3. Mass spectrum of the volatile compounds of rehydrated diced red bell peppers obtained by proton transfer reaction–mass spectrometry.

conditions causing fragmentation of certain compounds had the advantage that compounds such as 2-methylbutanal and 3-methylbutanal could be separated. Yeretzian et al. [14] reported efficient use of differences in break-up patterns of propanal and acetone (both M58). They varied the voltage between the last drift segment and the end plate of the drift tube to induce fragmentation via collisions with the background gas. Propanal and acetone showed very distinct fragmentation patterns.

Basically all 10 odour active compounds of the bell peppers were detected (Table 4), although the isobaric compounds 1-octen-3-one and dimethyl trisulphide could either not be separated or not be detected for threshold reasons. The five odour active compounds present in highest concentrations were 3-methylbutanal (84 nL L^{-1}), 2-methylbutanal (72 nL L^{-1}), hexanal (38 nL L^{-1}), 2-methylpropanal (20 nL L^{-1}) and diacetyl (8 nL L^{-1}). Four of the compounds coincide with the five odour active compounds with highest TIC in GC–MS analysis or FID peak area in GC–FID analysis. The 2- and 3-methylbutanal, as well as 2-methylpropanal showed large response in APCI–TOFMS analysis too.

3.6. Dynamic headspace analysis: comparison of techniques

The relative responses to the detected odour active compounds were calculated in order to compare the semi-quantitative results of the GC–MS, GC–FID, APCI–TOFMS and PTR–MS analyses (Fig. 4). A mutual pattern can be distinguished, with 2-methylpropanal, and 2- and 3-methylbutanal being the major odour active compounds in quantity. Most differences were observed for the compounds present in the lower concentration range. GC–FID showed a relatively low response to diacetyl and 1-penten-3-one. The GC–MS and PTR–MS patterns demonstrated large similarity, except for 1-octen-3-one/dimethyl sulphide. APCI–TOFMS is slightly different, with diacetyl missing and a low hexanal response. Compounds, such as 1-penten-3-one and 1-octen-3-one/dimethyl trisulphide, demonstrated

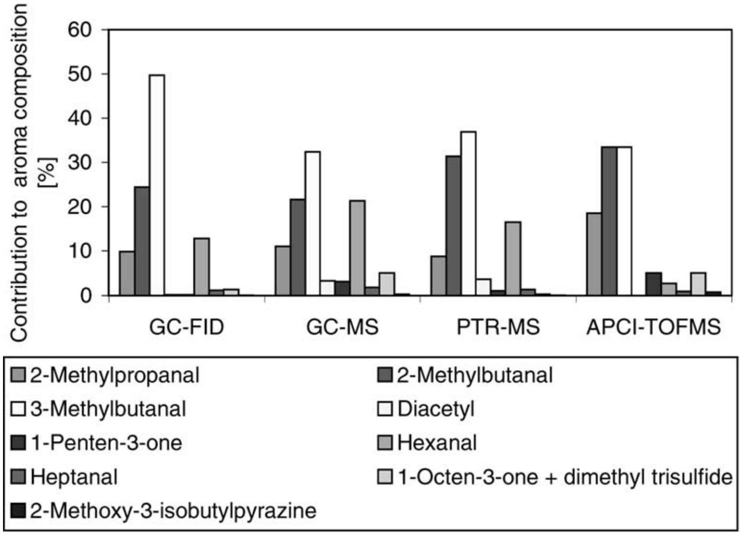

Fig. 4. Proportions of individual odour active compounds contributing to the aroma of rehydrated diced red bell peppers determined by GC–MS, GC–FID, APCI–TOFMS and PTR–MS.

relatively larger percentages in APCI–TOFMS. The relative contributions of the compounds were ranked (Table 5). The four techniques resulted in similar patterns for the odour active compounds, but APCI was slightly different. The two GC methods showed high correlation ($\rho = 0.946$), whereas the two direct MS techniques did not correlate very well ($\rho = 0.613$). When comparing the GC and MS analysis techniques with each other, they correlated significantly with one another, except the two direct MS techniques (Spearman's ranked correlation test, $P < 0.05$). However, at 1% significance level, APCI–TOFMS

Table 5
Ranks of proportions of odour active compounds contributing to the total aroma composition determined by four analysis techniques

Compound	GC–MS[a]	GC–FID[a]	APCI–TOFMS[a]	PTR–MS[a]
2-Methylpropanal	4	4	3	4
2-Methylbutanal	2	2	1.5	2
3-Methylbutanal	1	1	1.5	1
Diacetyl	6	7.5	9	5
1-Penten-3-one	7	7.5	4	7
Hexanal	3	3	6	3
Heptanal	8	6	7	6
1-Octen-3-one + dimethyl trisulphide[a]	5	5	5	8
2-Methoxy-3-isobutylpyrazine	9	9	8	9
P[b] (correlation with GC–MS)	–	0.946[*,**]	0.746[*]	0.883[*,**]
P (correlation with GC–FID)	–	–	0.775[*]	0.871[*,**]
P (correlation with PTR–MS)	–	–	0.613	–

Relative contributions are presented in Fig. 4.

[a] GC–MS: gas chromatography–mass spectrometry, GC–FID: gas chromatography–flame ionisation detection, APCI–TOFMS: atmospheric pressure chemical ionisation–time-of-flight mass spectrometry, PTR–MS: proton transfer reaction–mass spectrometry.

[b] Spearman's ranked correlation coefficient.

[*] Significant ranked correlation $P < 0.05$; [**] Significant ranked correlation $P < 0.01$.

did not show significant correlation with any of the other techniques.

4. Conclusions

GC–MS, GC–FID and PTR–MS analyses resulted in no significant different proportions of aroma compounds of rehydrated red diced bell peppers. APCI–TOFMS demonstrated more variant results as it correlated less significantly with the other techniques.

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