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LWT - Food Science and Technology 106 (2019) 122–127

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Short communication

A cool comparison of black and white pepper grades

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ARTICLE INFO

Keywords:
Adulteration
Fraud
PTR-MS
Quality
Volatiles

ABSTRACT

Black pepper (BP) is globally the most widely used spice and is appreciated for its aroma and taste qualities. Its aroma is influenced by various factors. In the current study, we examined a reference set of 90 quality BP and 40 quality white pepper (WP) samples from the EU spice industry for their volatile organic compounds (VOC) by Proton Transfer Reaction - Mass Spectrometry, as well as 10 low-grade pepper (LG) samples (light berries, rejects, spent). Furthermore, 50 retail BP and 30 WP samples were compared with the reference set. The predominant VOC measured were terpenes. BP presented the most abundant VOC profiles, followed by the WP group, and - at some distance - by the LG pepper material. Reference BP exhibited significantly higher intensities for 41% of the masses compared to WP, and the LG group lower intensities than both BP and WP for 27% of the masses. When using mass 137, the monoterpenes marker, retail samples presented significantly lower VOC intensities than their reference counterparts in case of 42% of the retail BP and 70% of the WP samples. Those samples may have suffered from poor storage conditions during production or potential adulteration or substitution with LG material.

1. Introduction

Piper nigrum L. is commonly known as black pepper (BP) and is the most widely used spice crop in the world (Abdulazeez, Sani, James, & Abdullahi, 2016). The pepper plant is a climbing, flowering vine and the peppercorn is the almost mature berry of the plant. Although indigenous to India, it is also cultivated in other tropical regions, such as Brazil, China, Indonesia, Madagascar, Malaysia, Mexico, Sri Lanka, Thailand, and Vietnam (Meghwal & Goswami, 2012; Prabhakaran Nair, 2011). BP has been used to flavour foods for millennia and is also know for the treatment of diseases. Because the spice was considered so precious, historically, BP was referred to as “The Black Gold”. BP constitutes one third of the global spice production (Thadchaigeni, Wijesinghe, Weerahewa, & Marambe, 2014); the latter representing a value of approximately 15 billion euro annually (Statista, 2018).

The pepper berries have a green colour. Their well-known black colour, is due to the enzymatic oxidation of polyphenolic substrates present in the skin of green pepper. White pepper (WP) is produced from BP by removal of the outer skin (Prabhakaran Nair, 2011). This decortication is conducted either by fermentation by lowering them in bags in streams or by mechanical methods that grind off the outer layer (Pradeepkumar, 2008). The oil fraction of the pepper – the essential oil or oleoresin - is extracted from dry powdered peppercorns, and is of great commercial value (Wang et al., 2018). In addition to good quality pepper, there are also lower grades (LG) such as light berries, rejects from the spiral separator (material that is broken, battered or lighter than others), and husks/skin from the WP production. Moreover, there are large volumes of extracted material (spent) from the essential oil production on the market. These materials are inferior in regard to sensory quality compared to quality BP and WP, which is also reflected by their price. Swapping or mixing of these grades can happen accidentally and intentionally. However, distinction between grades is not straightforward, especially when present in the ground form, due to the genetic similarities.

In the current study, we explored reference quality BP and WP, as well as LG material from the spice industry for their volatile organic compound (VOC) compositions by Proton Transfer Reaction - Mass Spectrometry (PTR-MS). Furthermore, we compared sets of retail BP and WP samples from various countries in the EU with the reference material.

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https://doi.org/10.1016/j.lwt.2019.02.054
Received 2 November 2018; Accepted 17 February 2019
Available online 20 February 2019
0023-6438/

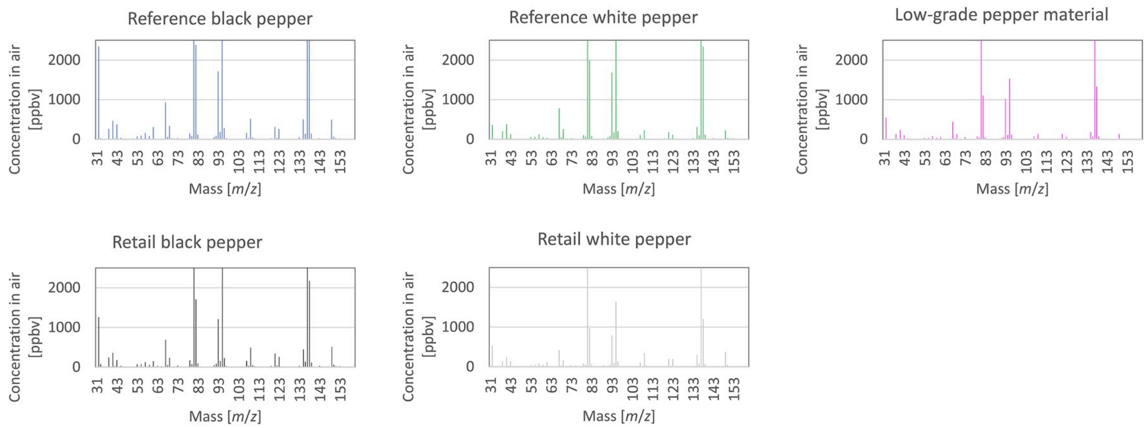

Fig. 1. Mean Proton Transfer Reaction – Mass Spectrometry profiles of reference black (n = 90) and white pepper (n = 40), LG material (n = 10), as well as retail black (n = 40) and white pepper (n = 30).

2. Materials and methods

2.1. Sample material

Ninety samples of quality BP produced in Brazil, India, Indonesia, Malaysia, Sri Lanka, and Vietnam from 2014 to 2017 were provided directly by seven European spice companies, and these served as reference materials. Similarly, 40 quality WP samples from Indonesia, Malaysia and Vietnam were collected as well as ten samples of LG material, which comprised below standard light berries, peel, pin heads, spiral rejects, broken/extracted material, and four additional kinds of spent material. Moreover, 50 ground BP samples were collected from retail outlets in Denmark, France, Germany, Ireland, Italy, Portugal, Spain, Switzerland, the Netherlands, and the UK as well as 30 WP samples in France, Ireland, Italy, Portugal, Spain, Switzerland, the Netherlands, and the UK. The latter were analysed before their sell-by dates.

2.2. Fingerprints of volatile compounds: PTR-MS

Sample material (100 mg ground material) was transferred into a 250 mL flask, which was capped and equilibrated in a water bath at 25 °C for 30 min. The headspace of the samples was subsequently analysed, in triplicate, by PTR-MS as described previously (Silvis, Luning, Klose, Jansen, & van Ruth, 2019). The headspace concentrations of the compounds were calculated as described by Hansel et al. (1995) and background and transmission corrections were applied. Subsequently, three mass spectra acquisitions of each of the three replicates of each sample were averaged to obtain a mean mass spectrum per sample. In this manner, a data matrix comprising mean mass spectra for all samples was compiled.

2.3. Statistical analyses

Means and standard deviations were calculated across each sample group, coefficients of variation were subsequently calculated by dividing the standard deviation of each mass by the mean of each mass (separately for the groups) and subsequent multiplication by 100%. Overall coefficients of variance (CV%) were determined by averaging the coefficients of variation across all masses for each sample group. In order to investigate the significance of differences between the groups and considering the non-normal distributions, the mass peak intensities from the PTR-MS analysis were subjected to Mann-Whitney and Kruskall-Wallis tests; the latter was followed by multiple pairwise comparisons using Dunn's procedure (XLstat 2017; Addinsoft, New York, USA). Frequency distributions and 1% percentiles were calculated for mass m/z 137 (XLstat 2017). A significance level of $p = 0.01$ was used throughout the study. Principal Component Analysis (PCA) was applied to visualize any natural clustering of the samples (no data preprocessing; Pirouette 4.0 Software, Infometrix, Seattle, WA, USA).

3. Results and discussion

3.1. Reference BP, WP and LG materials

The reference BP and WP samples, and the LG material, were subjected to PTR-MS analysis. The mean mass spectra of the VOCs are presented in Fig. 1 and the mean mass intensities are listed in Table 1. The identities of the VOCs of BP and WP were tentatively identified in our previous study (Silvis et al., 2019). Comparison with current data reveals that in BP and WP, the groups of monoterpenes and sesquiterpenes dominated the profiles and are represented by their parent masses and fragments, such as mass 81, 93, and 137. This is in agreement with studies of Jeleń and Gracka (2015) who reported an extensive list of terpenes in BP. Terpenes usually exhibit low sensory thresholds and thus contribute to the aroma. Although PTR-MS cannot distinguish between different monoterpenes because of their identical (molecular) mass, compounds likely to be present are limonene, linalool, myrcene, and pinene (Jeleń & Gracka, 2015). Furthermore, acetaldehyde (mass 45), acetic acid (mass 61), isoprene (mass 69), and estragol (mass 149) were found to contribute considerably to the VOC profile of the reference pepper samples as well. These compounds may

Table 1
Comparison of mass intensities of reference black (BP, $n = 90$) and white pepper (WP, $n = 40$) as well as LG pepper (LG, $n = 10$) material measured by Proton Transfer – Mass Spectrometry (mean ± standard deviation). Letters following intensity values for a particular mass indicate significant differences across sample groups (Kruskal-Wallis test followed by multiple pairwise comparisons using Dunn's procedure, $p < 0.01$).

Mass [m/z]	BP [ppbv]	WP [ppbv]	LG [ppbv]	Mass [m/z]	BP [ppbv]	WP [ppbv]	LG [ppbv]	Mass [m/z]	BP [ppbv]	WP [ppbv]	LG [ppbv]
31	7 ± 3b	3 ± 3 ab	3 ± 4a	76	0 ± 0b	0 ± 0b	0 ± 0a	119	25 ± 22a	23 ± 17a	16 ± 22a
33	2312 ± 1595b	363 ± 656a	545 ± 731a	77	5 ± 5 ab	5 ± 3b	3 ± 5a	120	6 ± 6b	4 ± 3 ab	3 ± 4a
34	27 ± 19b	5 ± 8a	6 ± 8a	78	2 ± 2 ab	2 ± 1b	1 ± 2a	121	308 ± 309b	184 ± 142a	139 ± 222a
35	5 ± 3b	1 ± 1a	1 ± 1a	79	142 ± 158b	106 ± 72b	74 ± 117a	122	32 ± 32b	19 ± 15a	14 ± 23a
36	0 ± 0b	0 ± 0a	0 ± 0 ab	80	78 ± 91 ab	66 ± 48b	48 ± 80a	123	257 ± 204b	114 ± 89a	65 ± 87a
38	0 ± 0a	1 ± 0a	0 ± 0a	81	29702 ± 21449b	25232 ± 10339b	13778 ± 15876a	124	25 ± 20b	11 ± 9a	6 ± 9a
39	258 ± 209b	204 ± 117b	130 ± 175a	82	2360 ± 2147b	1991 ± 988b	1105 ± 1463a	125	4 ± 2b	2 ± 1a	1 ± 1a
40	8 ± 6b	6 ± 4b	4 ± 6a	83	120 ± 92b	85 ± 43b	48 ± 59a	126	0 ± 0b	0 ± 0a	0 ± 0a
41	462 ± 304b	381 ± 170b	232 ± 267a	84	5 ± 3b	3 ± 1a	2 ± 2a	127	3 ± 3b	1 ± 1a	1 ± 1a
42	23 ± 15b	20 ± 14b	11 ± 13a	85	3 ± 2b	2 ± 1a	2 ± 2 ab	128	0 ± 0b	0 ± 0a	0 ± 0a
43	371 ± 195b	129 ± 45a	103 ± 59a	86	0 ± 0b	0 ± 0a	0 ± 0a	129	1 ± 1b	1 ± 0 ab	0 ± 1a
44	9 ± 5b	4 ± 1a	3 ± 2a	87	6 ± 4b	2 ± 1a	2 ± 1a	130	0 ± 0a	0 ± 0a	0 ± 0a
45	37 ± 20b	17 ± 10a	24 ± 15 ab	88	0 ± 0b	0 ± 0a	0 ± 0a	131	2 ± 3b	1 ± 1b	1 ± 1a
46	2 ± 1b	1 ± 1a	1 ± 0a	89	5 ± 6b	19 ± 19c	1 ± 1a	132	1 ± 1b	0 ± 0 ab	0 ± 0a
47	19 ± 12b	11 ± 9a	11 ± 14a	90	0 ± 0b	1 ± 1c	0 ± 0a	133	47 ± 34b	29 ± 16 ab	17 ± 16a
48	1 ± 0b	1 ± 0 ab	0 ± 0a	91	55 ± 40b	53 ± 27b	32 ± 38a	134	8 ± 6b	6 ± 3 ab	4 ± 4a
49	0 ± 0b	0 ± 0 ab	0 ± 0a	92	87 ± 98 ab	80 ± 56b	55 ± 85a	135	499 ± 398b	309 ± 177a	190 ± 242a
50	2 ± 2b	2 ± 1b	1 ± 1a	93	1688 ± 1184 ab	1685 ± 837b	1016 ± 1195a	136	139 ± 164b	99 ± 81b	71 ± 126a
51	18 ± 9b	8 ± 4a	5 ± 6a	94	186 ± 166 ab	171 ± 94b	111 ± 150a	137	24894 ± 20116b	20724 ± 9719b	11493 ± 13988a
52	1 ± 0b	1 ± 0 ab	0 ± 0a	95	3620 ± 3266b	2687 ± 1355b	1531 ± 2077a	138	2851 ± 2751b	2342 ± 1299b	1331 ± 1813a
53	72 ± 69b	57 ± 37b	36 ± 55a	96	278 ± 261b	205 ± 107b	118 ± 164a	139	145 ± 141b	118 ± 67b	69 ± 93a
54	3 ± 3b	2 ± 1b	1 ± 2a	97	27 ± 18b	15 ± 8a	9 ± 10a	140	5 ± 4b	4 ± 2b	2 ± 3a
55	93 ± 61b	59 ± 30a	34 ± 41a	98	2 ± 1b	1 ± 0a	1 ± 0a	141	1 ± 0a	0 ± 0a	0 ± 0a
56	4 ± 3b	3 ± 1a	2 ± 2a	99	3 ± 2b	1 ± 1a	1 ± 1a	142	0 ± 0b	0 ± 0 ab	0 ± 0a
57	160 ± 127b	124 ± 61b	77 ± 82a	100	0 ± 0b	0 ± 0a	0 ± 0a	143	2 ± 4a	1 ± 1a	1 ± 1a
58	7 ± 6b	5 ± 3 ab	3 ± 4a	101	1 ± 1b	1 ± 0a	1 ± 0a	144	0 ± 0a	0 ± 0a	0 ± 0a
59	85 ± 47b	47 ± 24a	38 ± 39a	102	0 ± 0b	0 ± 0a	0 ± 0a	145	1 ± 2b	1 ± 1b	1 ± 1a
60	3 ± 2b	2 ± 1a	1 ± 1a	103	2 ± 1b	4 ± 4c	1 ± 1a	146	0 ± 1b	0 ± 0 ab	0 ± 0a
61	305 ± 206b	37 ± 34a	65 ± 37a	104	0 ± 0 ab	0 ± 0b	0 ± 0a	147	10 ± 12b	5 ± 4a	4 ± 6a
62	7 ± 5b	1 ± 1a	2 ± 1a	105	11 ± 12b	6 ± 5a	5 ± 8a	148	7 ± 8b	3 ± 3a	3 ± 4a
63	2 ± 1b	1 ± 0a	1 ± 0a	106	3 ± 3a	2 ± 1 ab	1 ± 2a	149	491 ± 400b	223 ± 166a	134 ± 164a
64	0 ± 0b	0 ± 0a	0 ± 0a	107	158 ± 164b	105 ± 75 ab	74 ± 124a	150	59 ± 49b	27 ± 20a	16 ± 19a
65	10 ± 8b	8 ± 4b	5 ± 6a	108	29 ± 35b	21 ± 16b	16 ± 27a	151	26 ± 13a	22 ± 13a	15 ± 13a
66	5 ± 3b	4 ± 2b	2 ± 3a	109	512 ± 397b	227 ± 164a	133 ± 169a	152	3 ± 2a	3 ± 1a	2 ± 2a
67	924 ± 802b	782 ± 395b	439 ± 601a	110	47 ± 36b	21 ± 16a	14 ± 19a	153	21 ± 11b	21 ± 11 ab	14 ± 14a
68	58 ± 50b	50 ± 25b	29 ± 39a	111	23 ± 12b	12 ± 6a	7 ± 8a	154	3 ± 2a	3 ± 1a	2 ± 2a
69	335 ± 250b	256 ± 115b	141 ± 175a	112	2 ± 1b	1 ± 1a	1 ± 1a	155	6 ± 4b	3 ± 2a	4 ± 3 ab
70	19 ± 14b	14 ± 7b	8 ± 10a	113	2 ± 1b	1 ± 1a	1 ± 1a	156	1 ± 0b	0 ± 0a	0 ± 0 ab
71	22 ± 19b	17 ± 6b	9 ± 9a	114	0 ± 0b	0 ± 0a	0 ± 0a	157	1 ± 1b	0 ± 0 ab	0 ± 1a
72	1 ± 1b	1 ± 0b	1 ± 1a	115	1 ± 1b	0 ± 0a	0 ± 0a	158	0 ± 0a	0 ± 0a	0 ± 0a
73	30 ± 29a	31 ± 26 ab	57 ± 39b	116	0 ± 0b	0 ± 0b	0 ± 0a	159	1 ± 1b	0 ± 0 ab	0 ± 0a
74	2 ± 1a	2 ± 1a	3 ± 2a	117	1 ± 2b	3 ± 2c	1 ± 1a	160	0 ± 0a	0 ± 0a	0 ± 0a
75	6 ± 7b	9 ± 11b	1 ± 1a	118	0 ± 0a	0 ± 0b	0 ± 0a				

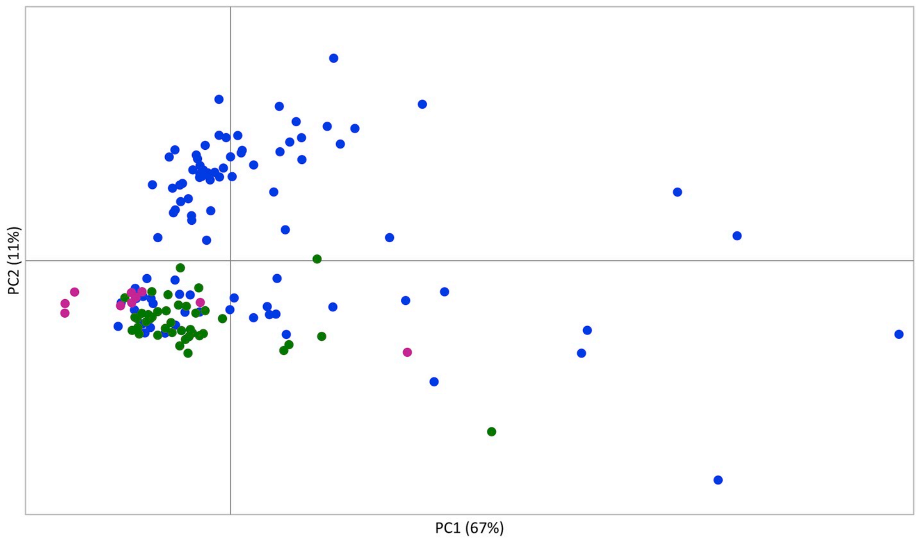

Fig. 2. Plot of the first two dimensions of Principal Component Analysis of the Proton Transfer Reaction – Mass Spectrometry profiles (no data pre-processing applied) of 90 reference black pepper samples (blue), 40 reference white pepper (green) and 10 LG material samples (pink). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

add top notes to the aroma, such as a green apple (acetaldehyde), pungent/sour (acetic acid), faint odour (isoprene), and sweet liquorice (estragol) notes (Silvis et al., 2019).

In order to evaluate the entire VOC profiles, the spectral data were also subjected to PCA (Fig. 2). The BP group spreads out over the first two dimensions, whereas the WP and LG samples cluster. The clusters present negative scores in the first and second dimension and overlap with a few BP samples. Generally, higher concentrations of VOCs were measured in the BP compared to the WP samples, and the latter were found to have in turn higher concentrations than LG material (Table 1). The significance of the differences in mass intensities between the groups was further examined by Kruskal-Wallis tests followed by multiple pairwise comparisons using Dunn's procedure ($p < 0.01$). The intensities of 52 of the 128 masses (41%) were significantly higher for the BP samples compared to the WP, and included all predominant masses. The intensities of 34 masses (27% of all masses) were significantly lower in the LG material compared to both reference BP and WP groups, but none were higher. This lower intensity reflects the extraction of essential oils or general lower VOC content of the material. Only five minor masses distinguished the three groups simultaneously: mass 89 (butanoic acid), 90 (its isotope), 103 (ethyl proprionate) and 117 (methyl isovalerate) (Silvis et al., 2019). For all of these five masses, highest concentrations were measured in WP, subsequently in BP, and followed by LG. The higher levels of the mentioned acids and their esters are possibly due to their formation during the fermentation process. The difference in nature in the LG material group is reflected by its CV%, which amounted 116% across the samples, whereas the values for BP and WP totalled 85% and 68%, respectively.

In summary, the BP group showed the most abundant VOC profiles, which is followed by the WP group, and then by the LG material. BP and WP sample groups were - overall - also more uniform in VOC intensities than the LG group.

3.2. Retail BP and WP compared with the reference materials

The sets of retail BP and WP samples were analysed by PTR-MS in addition to the reference samples (Fig. 1, Table 2) and results were compared with the reference and LG material of section 3.1. For 71 of the 128 masses (55%) significantly lower intensities were determined for the retail BP group compared to the reference BP group (Mann-Whitney test, $p < 0.01$). Similarly, 57 of the 128 masses (44%) displayed significantly lower concentrations for the retail WP group compared to its reference counterpart. The significantly different masses include the predominant masses related to the mono- and sesquiterpenes. On the other hand, 9 and 4 masses exhibited significantly higher concentrations in the retail BP and WP, respectively, in comparison to the reference material. These masses were low in concentration in general, except for mass 33 (methanol) which was present at substantial levels (~300–500 ppbv). This mass was present in higher concentrations in the retail WP than in the reference WP. Similarly, it was also higher in the LG material. The higher concentration may point at residue of extraction processes. Relative variation in the retail sample groups was higher than in their counterpart reference groups: the CV% of BP amounted 122% and the CV% of WP 102%.

Since many masses displayed similar differences between the sample groups, and terpenes are key volatiles of BP and WP, further comparison focused on mass 137, the parent ion of the monoterpenes which was the predominant mass in all samples. The frequency distributions of mass 137 for the various groups are shown in Fig. 3. The reference BP and WP show distributions from ~10,000 ppbv and up, whereas 40% of the LG material exhibit concentrations below this threshold. When comparing these frequency distributions with those of retail BP and WP, a surprisingly high proportion of the retail samples manifested themselves below this threshold as well. When considering 1% percentiles, this study found that 21 out of the 50 BP retail samples (42%) present mass 137 concentrations below the 1% percentile limit of

Table 2
Comparison of mass intensities of retail black (BP, $n = 40$) and white pepper (WP, $n = 30$) measured by Proton Transfer Reaction – Mass Spectrometry (mean ± standard deviation). Significant differences between retail and reference samples are indicated by the colours blue and orange: blue indicates intensity of retail samples < reference samples and orange indicates intensity of the retail samples > reference samples, blank boxes indicate no significant differences (Mann-Whitney test, $p < 0.01$).

Mass [m/z]	BP [ppbv]	WP [ppbv]	Mass [m/z]	BP [ppbv]	WP [ppbv]	Mass [m/z]	BP [ppbv]	WP [ppbv]
31	6 ± 7	3 ± 2	76	0 ± 0	1 ± 1	119	26 ±33	15 ± 18
33	1259 ± 1620	521 ± 382	77	6 ± 9	3 ± 4	120	7 ±6	5 ± 5
34	74 ± 306	6 ± 4	78	3 ± 3	2 ± 2	121	343 ±356	196 ± 204
35	3 ± 3	1 ± 1	79	170 ± 241	75 ± 95	122	36 ±38	21 ± 21
36	0 ± 0	0 ± 0	80	75 ± 110	42 ± 58	123	255 ±157	193 ± 159
38	0 ± 0	0 ± 0	81	19079 ± 25088	11843 ± 13606	124	25 ±15	19 ± 15
39	241 ± 290	140 ± 151	82	1711 ± 2466	968 ± 1210	125	3 ±2	2 ± 2
40	8 ± 9	4 ± 5	83	94 ± 97	62 ± 59	126	0 ±0	0 ± 0
41	359 ± 381	244 ± 232	84	4 ± 3	3 ± 2	127	2 ±2	1 ± 1
42	24 ± 31	14 ± 12	85	2 ± 1	1 ± 1	128	0 ±0	0 ± 0
43	178 ± 145	138 ± 106	86	0 ± 0	0 ± 0	129	1 ±2	0 ± 0
44	5 ± 4	4 ± 3	87	3 ± 3	1 ± 2	130	0 ±0	0 ± 0
45	31 ± 25	19 ± 12	88	0 ± 0	0 ± 0	131	2 ±4	1 ± 1
46	1 ± 1	0 ± 0	89	3 ± 4	35 ± 50	132	1 ±1	0 ± 0
47	15 ± 16	17 ± 25	90	0 ± 0	2 ± 2	133	28 ±25	20 ± 17
48	0 ± 0	0 ± 1	91	48 ± 63	27 ± 30	134	7 ±6	5 ± 4
49	0 ± 0	0 ± 0	92	86 ± 122	51 ± 66	135	447 ±399	300 ± 272
50	2 ± 2	1 ± 2	93	1208 ± 1600	791 ± 897	136	135 ±188	77 ± 95
51	9 ± 9	6 ± 5	94	152 ± 215	92 ± 110	137	16699 ±23783	9791 ± 12218
52	1 ± 1	0 ± 0	95	2880 ± 3767	1634 ± 1876	138	2175 ±3253	1205 ± 1581
53	72 ± 99	37 ± 46	96	229 ± 304	128 ± 149	139	114 ±169	63 ± 82
54	3 ± 4	2 ± 2	97	23 ± 17	16 ± 13	140	4 ±5	2 ± 3
55	76 ± 60	53 ± 45	98	1 ± 1	1 ± 1	141	0 ±0	0 ± 0
56	4 ± 3	2 ± 2	99	2 ± 1	1 ± 1	142	0 ±0	0 ± 0
57	125 ± 156	80 ± 81	100	0 ± 0	0 ± 0	143	1 ±3	1 ± 1
58	6 ± 7	3 ± 3	101	1 ± 1	1 ± 1	144	0 ±0	0 ± 0
59	56 ± 53	45 ± 33	102	0 ± 0	0 ± 0	145	1 ±2	1 ± 1
60	2 ± 2	2 ± 1	103	2 ± 1	5 ± 6	146	0 ±1	0 ± 0
61	150 ± 134	116 ± 135	104	0 ± 0	0 ± 0	147	12 ±11	7 ± 7
62	4 ± 3	3 ± 3	105	13 ± 15	6 ± 6	148	9 ±6	6 ± 6
63	26 ± 178	1 ± 1	106	3 ± 3	2 ± 2	149	512 ±307	371 ± 308
64	1 ± 4	0 ± 0	107	157 ± 170	97 ± 98	150	62 ±38	45 ± 38
65	18 ± 57	5 ± 6	108	29 ± 38	17 ± 20	151	24 ±20	15 ± 10
66	5 ± 5	3 ± 3	109	491 ± 322	344 ± 283	152	3 ±3	2 ± 1
67	688 ± 918	418 ± 494	110	46 ± 32	32 ± 26	153	20 ±16	15 ± 12
68	44 ± 57	28 ± 32	111	19 ± 11	16 ± 12	154	3 ±2	2 ± 2
69	234 ± 258	159 ± 161	112	2 ± 1	1 ± 1	155	6 ±5	3 ± 3
70	13 ± 14	9 ± 9	113	1 ± 1	1 ± 1	156	1 ±1	0 ± 0
71	12 ± 12	11 ± 9	114	0 ± 0	0 ± 0	157	1 ±1	0 ± 0
72	1 ± 1	1 ± 0	115	1 ± 0	0 ± 0	158	0 ±0	0 ± 0
73	41 ± 23	36 ± 18	116	0 ± 0	0 ± 0	159	1 ±1	0 ± 0
74	2 ± 1	2 ± 1	117	1 ± 2	3 ± 5	160	0 ±1	0 ± 0
75	4 ± 4	29 ± 39	118	0 ± 0	0 ± 0			

the reference BP samples (5207 ppbv). Similarly, 21 of the 30 WP retail samples (70%) appear below the lower 1% percentile of mass 137 of the WP samples (10,695 ppbv). This indicates that the VOC intensity of those retail samples is below those of the reference samples provided by the spice industry, based on the application of mass 137 as a marker compound. This may be due to mixing of high and low quality raw materials, extensive ageing or poor storage conditions, - although the sell-by dates of all retail products had not expired. Consequently, a large proportion of the pepper sold in retail outlets across Europe differs considerably from the material that is considered the required quality by the spice industry.

4. Conclusions

Analysis of large reference sets of BP and WP revealed that BP is most abundant in VOCs, followed by the WP group, and at some distance by the LG group. A considerable fraction of the retail BP (42%) and WP (70%) samples sourced in the EU exhibit significantly poorer VOC profiles than the industry supplied materials which were considered the correct quality. Some of those retail samples may have been of appropriate quality but their quality decreased over time. However, the similarity in terms of quality of some of these samples to LG material was striking. This study has pointed to the need for increased

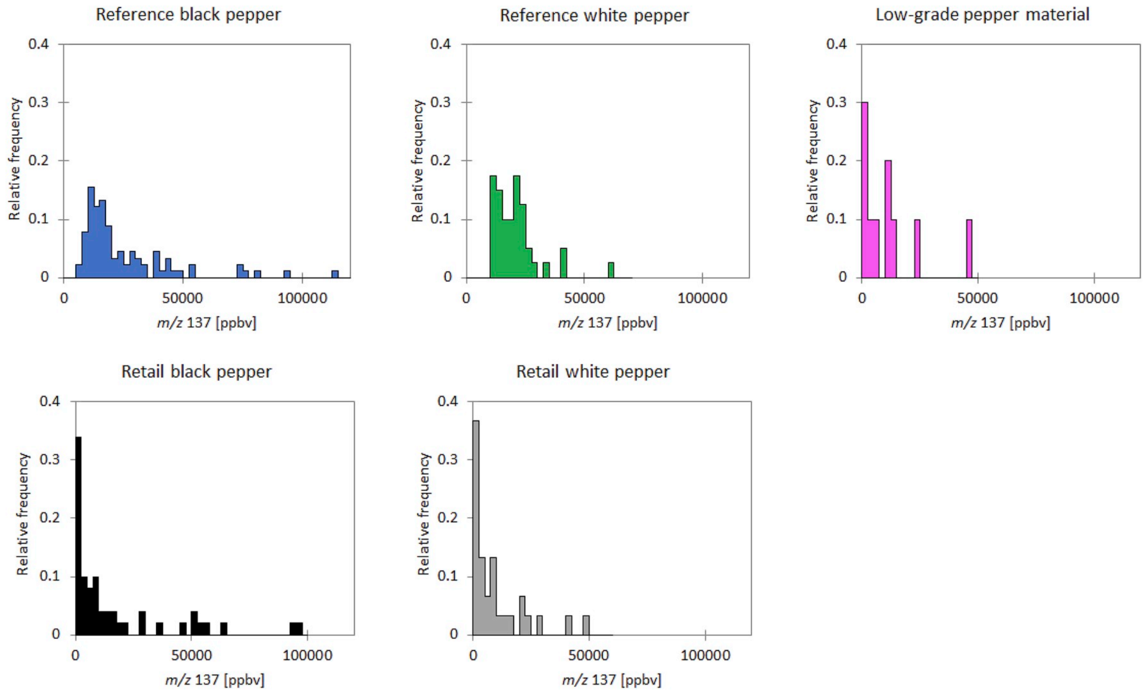

Fig. 3. Frequency distributions of mass 137 for reference black (n = 90) and white pepper (n = 40), LG material (n = 10), as well as retail black (n = 40) and white pepper (n = 30).

awareness and control of quality and fraud by the spice industry supply chains and regulatory authorities.

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