



## Authenticity of raspberry flavor in food products using SPME-chiral-GC-MS

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## Authenticity of raspberry flavor in food products using SPME-chiral-GC-MS

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| Search Terms:                 | Authenticity, SPME, raspberry flavor, chiral-GC-MS  |
| Abstract:                     | <p>A fast and simple method for authenticating raspberry flavors from food products was developed. The two enantiomers of the compound (E)-<math>\alpha</math>-ionone from raspberry flavor were separated on a chiral gas chromatographic column. Based on the ratio of these two enantiomers the naturalness of a raspberry flavor can be evaluated due to the fact that a natural flavor will consist almost exclusively of the R enantiomer, while a chemical synthesis of the same compound will result in a racemic mixture. 27 food products containing raspberry flavors were investigated using SPME-chiral-GC-MS. We found raspberry jam, dried raspberries and sodas declared to contain natural aroma all contained almost only R-(E)-<math>\alpha</math>-ionone supporting the content of natural raspberry aroma. Six out of eight sweets tested did not indicate a content of natural aroma on the labelling which was in agreement with the almost equal distribution of the R and S isomer. Two products were labelled to contain natural raspberry flavors but were found to contain almost equal amounts of both enantiomers indicating a presence of synthetic raspberry flavors only. Additionally, two products labelled to contain both raspberry juice and flavor showed equal amounts of both enantiomers, indicating the presence of only synthetic flavor.</p> |

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4 **Running head:** Authenticity of raspberry flavor SPME-chiral-GC-MS

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10

## 11 **Abstract**

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13 of the compound (E)- $\alpha$ -ionone from raspberry flavor were separated on a chiral gas chromatographic column. Based on  
14 the ratio of these two enantiomers the naturalness of a raspberry flavor can be evaluated due to the fact that a natural  
15 flavor will consist almost exclusively of the R enantiomer, while a chemical synthesis of the same compound will result  
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21 to contain natural raspberry flavors but were found to contain almost equal amounts of both enantiomers indicating a  
22 presence of synthetic raspberry flavors only. Additionally, two products labelled to contain both raspberry juice and  
23 flavor showed equal amounts of both enantiomers, indicating the presence of synthetic flavor.

24

25 **Keywords:** Authenticity, SPME, chiral-GC-MS, raspberry flavor,  $\alpha$ -ionone, enantioselective GC

## 26 Introduction

27 Authenticity of food products is often used as a parameter of quality in marketing. Food products containing only  
28 natural ingredients are preferred by many consumers who are willing to pay a higher price for such products. Natural  
29 aroma components are often more expensive than their synthetic equivalent making counterfeit an economical benefit.  
30 Counterfeit of aroma components is misleading of the consumers and is illegal according to European legislation  
31 (European Parliament 2008) where the term “Natural” can be used only for flavors containing exclusively natural  
32 flavoring substances. A natural flavor should be obtained by appropriate physical, enzymatic or microbiological  
33 processes from the material of vegetable, animal or microbiological origin (European Parliament 2008).

34 The flavor of raspberries consist of many different aroma compounds all contributing more or less to the characteristic  
35 perception of raspberries. Malowicki *et al.* investigated the volatile composition of raspberries following stir bar  
36 sorptive extraction and identified some 30 compounds including (Z)-hexenol, hexanal, (E)-2-hexenal, 2-heptanone,  $\delta$ -  
37 octalactone,  $\delta$ -decalactone, geraniol,  $\alpha$ -ionone,  $\beta$ -ionone and terpinen-4-ol as the major constituents (Malowicki *et al.*  
38 2008a and b). Some of the flavoring substances are chiral and the enantiomeric composition in raspberry extracts was  
39 characterized by chiral GC-MS,  $\alpha$ -ionone occurs mainly in the R-form (97-100%) whereas  $\delta$ -octalactone,  $\delta$ -decalactone  
40 and terpinen-4-ol occurs mainly in the S-form (80-100%) (Malowicki *et al.* 2008a and b). Also, Werkhoff *et al.* (1991)  
41 found an enantiomeric composition of  $\alpha$ -ionone in raspberry extract sampled by head space of 99.9% R-form and 0.1%  
42 S-form (Werkhoff *et al.* 1991). The enantiomeric composition of  $\alpha$ -ionone and  $\delta$ -decalactone in raspberry extract was  
43 by chiral GC determined to 98-100% R-form for ionone and to 98-100% S-form for decalactone (Casabianca and Graff  
44 1994). The enantiomeric composition of a number of chiral 4-alkylated- $\gamma$ -lactones from C<sub>5</sub> to C<sub>12</sub> were determined in  
45 extracts from apricot, mango, passion fruit, peach, raspberry and strawberry (Bernreuther *et al.* 1989. Guichard *et al.*  
46 1990). For all fruits there seemed to be a preponderance of the R-form of the longer chained  $\gamma$ -lactones > C<sub>8</sub> whereas for  
47 the shorter chained  $\gamma$ -lactones some fruits had preponderance of the R-form, some of the S-form and some hardly  
48 showed enantiomeric excess. In both orange flowers and unifloral orange honey the enantiomeric composition of  
49 linalool was 87-91% of the (+) form and 9- 13% of the (-) form indicating the usefulness of chiral analysis in the  
50 authenticity assessment of unifloral honey (Verzera *et al.*, 2014).

51 Ravid *et al.* (2010) assessed the authenticity of natural fruit compounds in food and beverages using head space  
52 SPME chiral GC-MS. The enantiomeric composition of linalool, linalyl acetate and limonene in were characterized in  
53 bergamot oil,  $\gamma$ -decalactone and  $\gamma$ -undecalactone in peach and nectarine products,  $\gamma$ -lactones in passion fruit products  
54 and  $\alpha$ -ionone in raspberry products. The study showed that (E)- $\alpha$ -ionone in raspberry is efficiently adsorbed on an  
55 SPME fiber and occur almost exclusively as the R enantiomer, whereas (E)- $\alpha$ -ionone originating from chemical  
56 synthesis is a racemic mixture containing almost equal amounts of both enantiomers. In raspberries the biosynthesis of  
57 (E)- $\alpha$ -ionone is catalyzed by stereospecific enzymes leading to a preponderance of (R)-(E)- $\alpha$ -ionone of more than 99%  
58 (Ravid *et al.* 2010). Consequently presence of (S)-(E)- $\alpha$ -ionone could be an indicator of adulteration with artificial  
59 aroma components (Aprea *et al.* 2009; Taylor & Linforth 2010).

60 Head space SPME is an attractive method to isolate and concentrate volatile compounds from complex samples such as  
61 foods because only little sample pretreatment is required. In this study we investigated three different fiber coatings:  
62 divinylbenzene/polydimethylsiloxane (DVB/PDMS), carboxen/polydimethylsiloxane (CAR/PDMS), and  
63 divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) for the capabilities to extract volatile compounds,  
64 from raspberry aroma and in particular (E)- $\alpha$ -ionone, as this compound is the major enantiomeric compound bound to  
65 the extraction fiber. Furthermore, addition of sodium chloride during head space SPME was investigated for potential  
66 improvement of extraction efficiency. Finally, 27 raspberry containing and/or flavored samples of foods, beverages and  
67 sweets from the Danish market were analyzed for enantiomer composition of (E)- $\alpha$ -ionone to investigate whether the  
68 labeling were in compliance with the EU regulation. The samples set included sodas and sweets, products which have  
69 not previously been investigated for authenticity.

## 70 **Materials and methods**

71 Samples: Samples of jam, sodas, sweets, dried raspberries, fruit bars and yoghurts from the Danish retail market were  
72 purchased at different retailers, all declared to contain raspberries, natural flavor and/or flavor, see Table 1. Samples of  
73 fresh raspberries were obtained from the local retail market. Chemicals: Pure standard of  $\alpha$ -ionone was purchased from  
74 Sigma-Aldrich (Steinheim, Germany). Sodium chloride was purchased from Merck (Darmstadt, Germany).

75 SPME fibers: SPME fibers were purchased from Supelco, (Supelco, USA), all coated on a fused silica fiber and with a  
76 length of 1cm; divinylbenzene (DVB)/polydimethylsiloxane (PDMS) 65 $\mu$ m coating, carboxen (CAR)/(PDMS) 75 $\mu$ m  
77 coating and DVB/CAR/PDMS 50 $\mu$ m DVB and 30 $\mu$ m CAR on PDMS coating.

78 SPME-chiral-GC-MS method: The SPME fibers were used for extracting aroma compounds from raspberries and  
79 subsequent analysis using automated headspace solid phase micro extraction (HS-SPME) using a GC-Combi PAL  
80 (CTC Analytical, Zwingen, Switzerland) on an Agilent 6890 gas chromatograph (GC) (Agilent Technologies, Inc.,  
81 Wilmington, Germany) equipped with an Agilent 5979 Mass Selective Detector.

82 Samples of fresh raspberries were macerated with a fork prior to transfer to the sample vials. No sample preparation,  
83 except homogenization was performed on jam, soda, yoghurt and dried raspberry samples. Sweets and the fruit bar were  
84 cut in 5 mm pieces prior to transfer to the sample vials. Approximately 4g of all samples was placed in a 10 mL  
85 headspace vial. The vial was heated to 60°C before the SPME fiber was exposed to the headspace. Extraction was  
86 carried out at 60°C for 30 min. using agitation. Optimized extraction conditions were adapted from Cagliero *et al.*  
87 (2012). Hereafter analytes were thermally desorbed into the GC inlet at 230°C for 5 minutes in splitless mode. The GC  
88 was used with the following temperature program: 50°C for 5 min. and then raised at 30°C/min. to 100°C and raised  
89 again at 2°C/min. to 145°C and finally 30°C/min. to 200°C for 4 min. (GC runtime: 35 min.). For the method  
90 optimizing part, the following temperature program was used: 50°C for 7 min. and then raised at 1.5°C/min. to 180°C  
91 and raised again at 6°C/min. to a final temperature of 200°C/min. for 5 min. (GC runtime: 102 min.). The column was  
92 a  $\beta$ -DEX 225 (Supelco, USA) consisting of non-bonded 25% 2,3-di-O-acetyl-6-O-TBDMS- $\beta$ -cyclodextrin in a SPB-20  
93 phase 0.25mm x 30m, 0.25 $\mu$ m film thickness. Carrier gas was helium at 0.8 ml/min, 33 cm/sec. The transfer line  
94 temperature was 250°C, MS source 230°C, MS Quad 150°C. The mass spectrometer was used in Electron Ionization  
95 (EI) mode using Scan mode ( $m/z$  40-400) for the method optimizing part using Nist library for identification of  
96 compounds. The mass spectrometer was operated in Single Ion Monitoring (SIM) for food samples, using  $m/z$  121 as  
97 quantifier ion and 192, 136 and 93 as qualifiers to ensure the identity and purity of the peaks. Quality ratio control of

98 the qualifiers were  $\pm 20\%$  and quality control of the retention time was  $\pm 0.2$  min.. Samples were analyzed as single  
99 determinations, which were deemed sufficient because percentages of R- $\alpha$ -ionone close to 100 in the samples would  
100 indicate natural flavor whereas values close to 50 would indicate synthetic flavor.

101 **Table 1.**

102

## 103 **Results and discussion**

104 Before analyzing the samples the analytical method were optimized in order to obtain a fast and reliable method for the  
105 documentation of the authenticity of raspberry flavor in food products. The optimization was performed using  
106 macerated raspberries as samples and included SPME fiber coating selection and the influence of addition of sodium  
107 chloride to the samples. A full scan SPME GC-MS chromatogram of macerated raspberries, using a DVB/CAR/PDMS  
108 fiber is shown in Figure 1, where it appears that  $\alpha$ -ionone and  $\beta$ -ionone are the highest peaks.

109 **FIG. 1**

110 To study the influence of fiber coating on the SPME the following fiber types were selected, all coated on a fused silica  
111 fiber and with a length of 1cm; divinylbenzene (DVB)/polydimethylsiloxane (PDMS) 65 $\mu$ m coating, carboxen  
112 (CAR)/(PDMS) 75 $\mu$ m coating and DVB/CAR/PDMS with 50 $\mu$ m DVB coating / 30 $\mu$ m CAR on PDMS coating.  
113 Macerated raspberries were used as a basis model for the experiments. For this method optimizing study, only the  
114 ability to extract analytes from raspberries was investigated and the levels where therefore not quantified but based on  
115 comparison of peak areas and presented in Figure 2.

116 **FIG. 2**

117 The three SPME fibers showed approximately similar abilities to extract the seven major chemical constituents from  
118 raspberry headspace. With the exception that octanol was not extracted by DVB/CAR/PDMS and CAR/PDMS. In  
119 addition  $\beta$ -phellandrene and nonanal were not extracted by CAR/PDMS. The DVB/CAR/PDMS fiber showed slightly  
120 better extraction efficiency for ionone and was therefore selected for the further studies.

121

122 **Influence of addition of sodium chloride to samples**

123 The effect of addition of sodium chloride to the matrix was investigated, as increased ionic strength usually improves  
124 the extraction efficiency of hydrophilic compounds (Kudlejova *et al.* 2012). Sodium chloride was added to the sample  
125 matrices to a concentration of 25 w/w % and analytes extracted with a SPME fiber coated with DVB/CAR/PDMS and  
126 presented in Figure 3.

127 **FIG. 3**

128

129 From Figure 3 it is clear that addition of sodium chloride does not have a positive effect upon extraction of the majority  
130 of the analytes from raspberries. On the contrary it looks like the salt has a negative effect on the extraction especially  
131 for  $\alpha$ -pinene, caryophyllene,  $\alpha$ - and  $\beta$ -ionone. For the other compounds analyzed the effect was less pronounced. Only  
132 the extraction of linalool was a little higher when sodium chloride was added. Pawliszyn 2012 reported that the positive  
133 effect of salt increases with increased polarity of the analytes, which is in agreement with the results found in this study  
134 (Pawliszyn 2012).

135 The result for  $\beta$ -ionone is in agreement with the results of Yang and Peppard, who found that the extraction of  $\beta$ -ionone  
136 decreases with higher sodium chloride concentrations when extracted with a SPME fiber, coated with 100  $\mu$ m PDMS  
137 (Yang and Peppard 1994).

138

### 139 **Content of R-(E)- $\alpha$ -ionone and S-(E)- $\alpha$ -ionone in foods, beverages and sweets from the Danish market**

140 For authenticity investigation of raspberry flavored foods using head space SPME chiral GC-MS the most important  
141 compound is  $\alpha$ -ionone. From the chromatogram in Figure 4 it can be seen that (S)- $\alpha$ -ionone is barely detectable in  
142 macerated raspberry (top) compared to the peak of (R)- $\alpha$ -ionone. This is in accordance with previously published  
143 results on the analyses of enantiomer ratios of  $\alpha$ -ionone in raspberries showing that (R)- $\alpha$ -ionone constitutes more than  
144 97% (Sewing *et al.*, 2005; Ravid *et al.* 2010). On the contrary synthetic raspberry aroma (Figure 4 bottom) shows the  
145 presence of both enantiomers in almost equal amounts. Synthetic  $\alpha$ -ionone can be added to natural raspberry flavor i.e.  
146 in order to fortify the flavor and/or reduce price. In that case the enantiomer ratio will not be 50:50, but reflect the  
147 percentage of synthetic aroma added to the natural raspberry aroma and it would still be possible to detect (S)- $\alpha$ -ionone  
148 indicating a not purely natural flavor.



149 **FIG. 4**

150 Twenty seven samples of food beverages and sweets from the Danish retail market were analyzed for enantiomer ratio  
151 of (E)- $\alpha$ -ionone using the described head space solid phase micro extraction method including chiral-gas  
152 chromatography combined with mass spectrometric detection using SIM mode. Table 1 present the results calculated as  
153 the percentage of R-(E)- $\alpha$ -ionone and S-(E)- $\alpha$ -ionone in all samples. Six samples of raspberry jam declared to contain  
154 between 35 and 50% fruit, all had a huge preponderance of the (R) enantiomer of  $\alpha$ -ionone with the (S) enantiomer  
155 being barely detectable. These jams were all declared not to have been added any aroma which the analyses confirmed.

156 Analyses of two out of five soda's declared to contain natural aroma only, showed that these contained only (R)- $\alpha$ -  
157 ionone which is in accordance with the declared content. The three soda's declared to contain aroma showed an  
158 enantiomer ratio of 50%, which is, also, in accordance with the declaration and confirm that synthetic  $\alpha$ -ionone had  
159 been added to the products.

160 The dried raspberries only contained the (R) enantiomer of  $\alpha$ -ionone, so no synthetic  $\alpha$ -ionone was added to this  
161 product. Six of the sweets samples had a 50:50 enantiomer ratio which is in accordance with the declared use of aroma  
162 in these samples. Two of the sweets were declared to contain raspberry juice concentrate, 5% as well as aroma.  
163 However, the content of ionone from this source must be very low as addition of raspberry juice containing exclusively  
164 the (R) enantiomer would have been expected to change the enantiomer ratio from the observed 50:50%. The fruit bar  
165 was declared to contain both 1.3% raspberry and natural aroma, however, the measured enantiomer ratio of 50:50%  
166 suggest that synthetic aroma was added to this product and accordingly the declaration is not compliant with  
167 legislation.

168 Finally, six yoghurt samples, declared to contain between 1.3% and 14% raspberries, were analyzed. Three of the  
169 samples were declared, in addition to raspberries, also to contain natural aroma. For five of the raspberry yoghurt  
170 samples only the (R) enantiomer of  $\alpha$ -ionone were found in the products indicating natural raspberries were used in the  
171 product. However, for yoghurt #3 declared to contain 1.7% raspberry and natural aroma, a 50:50 enantiomer ratio for  
172 R- $\alpha$ -ionone and S- $\alpha$ -ionone was observed indicating that synthetic  $\alpha$ -ionone was added as aroma to this product  
173 contrary to the declared use of natural aroma.

174

## 175 **Conclusions**

176 A fast and simple headspace SPME-chiral-GC-MS method for analyses of authenticity of l raspberry flavor in foods has  
177 been developed and used to analyze samples of jams, sodas, sweets, fruits bars, dried raspberries and yoghurts.  
178 Raspberry jam, dried raspberries and sodas declared to contain natural aroma all contained almost only R- $\alpha$ -ionone  
179 supporting the content of only naturally raspberry or naturally raspberry aroma used in the products. All sweets tested  
180 had an almost equal distribution between R- $\alpha$ -ionone and S- $\alpha$ -ionone indication that synthetic aroma was added to these  
181 products in agreement with the information from the declaration. For two out of the 27 products tested, the fruit bar and  
182 one of the raspberry yoghurts, both R- $\alpha$ -ionone and S- $\alpha$ -ionone was detected at an enantiomer ratio of 50% indicating  
183 the use of synthetic aroma in the products, which is in disagreement with the declared information on the products.

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186 have no conflict of interest to declare.

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231 **Table 1: Sample description and R-(E)- $\alpha$ -ionone and S-(E)- $\alpha$ -ionone analyses in food and sweet samples from the**  
 232 **Danish market.**

| Sample               | Fruit content declared | Natural aroma declared | Aroma declared | R- $\alpha$ -ionone % | S- $\alpha$ -ionone % | Compliance with EU legislation |
|----------------------|------------------------|------------------------|----------------|-----------------------|-----------------------|--------------------------------|
| Jam #1               | Raspberry, 35%         |                        |                | 97.1                  | 3.0                   | Yes                            |
| Jam #2               | Raspberry, 50%         |                        |                | 97.4                  | 2.6                   | Yes                            |
| Jam #3               | Raspberry, 50%         |                        |                | 96.8                  | 3.2                   | Yes                            |
| Jam #4               | Raspberry, 45%         |                        |                | 96.3                  | 3.7                   | Yes                            |
| Jam #5               | Raspberry, 40%         |                        |                | 98.5                  | 1.5                   | Yes                            |
| Jam #6               | Raspberry, 45%         |                        |                | 97.3                  | 2.7                   | Yes                            |
| Soda #1              |                        |                        | x              | 49.9                  | 50.1                  | Yes                            |
| Soda #2              |                        |                        | x              | 49.8                  | 50.2                  | Yes                            |
| Soda #3              |                        | x                      |                | 100                   | 0                     | Yes                            |
| Soda #4              |                        | x                      |                | 100                   | 0                     | Yes                            |
| Soda #5              |                        |                        | x              | 50.6                  | 49.4                  | Yes                            |
| Dried raspberries #1 | Dried fruits           |                        |                | 100                   | 0                     | Yes                            |
| Sweet #1, fruit gum  |                        |                        | x              | 49.9                  | 50.1                  | Yes                            |
| Sweet #2, fruit gum  |                        |                        | x              | 49.9                  | 50.1                  | Yes                            |
| Sweet #3, fruit gum  |                        |                        | x              | 49.7                  | 50.3                  | Yes                            |
| Sweet #4, fruit gum  | Raspberry juice        |                        | x              | 50.4                  | 49.6                  | ?                              |
| Sweet #5, fruit gum  | Raspberry juice        |                        | x              | 51.0                  | 49.0                  | ?                              |
| Sweet #6, lollipops  |                        |                        | x              | 50.4                  | 49.6                  | Yes                            |
| Sweet #7, fruit gum  |                        |                        | x              | 50.2                  | 49.8                  | Yes                            |
| Sweet #8, fruit gum  |                        |                        | x              | 50.4                  | 49.6                  | Yes                            |
| Fruit bar #1         | Raspberry 1.3%         | x                      |                | 49.2                  | 50.8                  | No                             |
| Yoghurt #1           | Raspberry 14%          |                        |                | 100                   | 0                     | Yes                            |
| Yoghurt #2           | Raspberry 7.5%         |                        |                | 100                   | 0                     | Yes                            |
| Yoghurt #3           | Raspberry 1.7%         | x                      |                | 49.5                  | 50.5                  | No                             |
| Yoghurt #4           | Raspberry 7%           | x                      |                | 100                   | 0                     | Yes                            |
| Yoghurt #5           | Raspberry 8%           | x                      |                | 100                   | 0                     | Yes                            |
| Yoghurt #6           | Raspberry 6%           |                        |                | 100                   | 0                     | yes                            |

233

234 **Figure legends**

235

236 **Figure1: Full scan head space SPME GC-MS chromatogram of macerated raspberries, GC runtime 102 min.**

237 **Figure2: Peak areas for 8 analytes extracted from raspberries with DVB/CAR/PDMS, DVB/PDMS, and**

238 **CAR/PDMS SPME fibers**

239 **Figure3: Peak area for 7 analytes extracted from raspberries with DVB/CAR/PDMS SPME fiber with and**

240 **without addition of NaCl.**

241 **Figure 4: Chromatograms of raspberry jam containing primarily R-(E)- $\alpha$ -ionone (top) and of yoghurt**

242 **containing synthetic raspberry aroma withboth R-(E)- $\alpha$ -ionone and S-(E)- $\alpha$ -ionone (bottom).**









