Supporting Information

Fiber-sample distance, an important parameter to be considered in headspace solid-phase microextraction (HS-SPME) applications.

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MATERIALS AND METHODS

Chemicals and reagents
Analytical standards of 3-methylbutanal (CAS. 590-86-3, MW 86.13 g/mol), 5-hexen-1-ol (CAS. 821-41-0, MW 100.16 g/mol), furfural (CAS. 98-01-1, MW 96.08 g/mol), linalool (CAS. 78-70-6, MW 154.25 g/mol), guaiacol (CAS. 90-05-01, MW 124.14 g/mol), pentane (CAS. 109-66-0, MW 72.15 g/mol), octadecane (CAS. 593-45-3, MW 254.49 g/mol), butanoic acid (CAS. 107-92-6, MW 88.11 g/mol), hexanoic acid (CAS. 142-62-1, MW 116.16 g/mol), decanoic acid (CAS. 334-48-5, MW 172.26 g/mol), 3-methylbutanoic acid (CAS. 503-74-2, MW 102.13 g/mol), D-limonene (CAS. 5989-27-5, MW 136.23 g/mol) and monobasic sodium phosphate (CAS. 10,049-25-5, MW 137.99 g/mol) were purchased from Sigma-Aldrich (Milan, Italy). Octanoic acid (CAS. 124-07-2, MW 144.21 g/mol) was supplied by Fluka (Germany). Standard stock solutions were prepared in Milli-Q water (Millipore, Bedford, MA, USA) and stored at 4°C. Individual working solutions were obtained by suitable dilution of standard stock solutions with Milli-Q water to obtain the desired concentrations.

HS-SPME experimental conditions
All extractions were carried-out using an autosampler PAL RSI 85 (Zwingen, Switzerland) allowing to reach the specific fiber penetration depths and reduce operator bias, working in accurate conditions with higher repeatability. Samples incubation were performed in a heat agitator set at an agitation speed of 250 rpm, with an on-time of 5 s and an off-time of 2 s. All the SPME fibers used were supplied by Supelco, (Bellefonte, PA, USA) and have a needle length of 1 cm, which was kept constant in all experiments. Fibers were inserted in HS vials at a speed of 20 mms⁻¹ and were conditioned before and after extraction in a desorption port at 260°C for 10 min.
Moreover, HS-SPME were also performed at higher stirring rates (400 and 550 rpm) to assess the effect of fiber-sample distance in higher agitation conditions. This range of stirring rates cover 79.6% of the HS-SPME experiments published in 2019. Indeed, in 200 research articles published in 2019, 51.5% did not specify the stirring rate, 17% were performed at 250 rpm, 11.5% were performed at 500 rpm, while 7% were performed without agitation, 3% were performed at 350 rpm, 3% at 600 rpm, 1% at 400 rpm, and 5.5% of the studies were performed using a stirring rate higher than 700 rpm (Table S1).
Stirring rates higher than 550 rpm were not advisable to avoid the fiber getting wet and damaged by the sample.
20 mL vial was chosen for HS-SPME because it is the most used vial volume in HS-SPME analysis. Once again, in 200 articles of 2019 in which HS-SPME was performed, more than 60% used a 20 mL vial (Table S1).

Fiber-sample distances
The fiber-sample distance refers to the distance between the tip of the SPME fiber and the sample surface. For a practical reason it is easier for the reader and the scientific community to indicate
either the depth of penetration of the fiber, which can be given with precision by an autosampler, or to precise the distance between the fiber tip and the top/surface of the sample (fiber-sample distance), which can be given by measuring this distance when extraction is performed manually.

**Gas chromatography-mass spectrometry (GC-MS) conditions**

GC-MS analyses were carried-out on an Agilent 7890B gas chromatograph system equipped with an autosampler (PAL RSI 85) and coupled to an Agilent 5977B mass selective detector (Santa Clara, California, USA). The carrier gas used was Helium, at a flow rate of 1.2 mL min\(^{-1}\). After extraction, the fiber was desorbed in an injection port equipped with a liner (800 µL) at a temperature of 260°C under splitless mode. The inlet penetration depth was 40 mm, at a speed of 100 mm s\(^{-1}\). The MSD transfer line was set at a temperature of 260°C. The MS source and quadrupole temperatures were 230 and 150°C, respectively. The gain factor was set at 0.05, while the resulting electron multiplier (EM) voltages were lower than 1300 V.

All VOCs separation was performed using a DB – Wax column (60 m, 0.25 mm i.d., 0.25 µm film thickness) (J&W Scientific, Folsom, CA, USA) following different oven temperature program gradients.

For the analyses of alkanes, the oven was maintained at 50°C for 4 min, then raised to 325°C at a rate of 15°C min\(^{-1}\), and held at 325°C for 4 min. Data were acquired in scan ion mode with a scan range of 29-400 m/z.

For the analyses of the 6 VOCs, the oven temperature was kept at 35°C for 4 min, then raised to 120°C at a rate of 5°C min\(^{-1}\), to 250°C at a rate of 16°C min\(^{-1}\) and held at 250°C for 1 min. For FFAs standards analyses, the initial oven temperature was 50°C for 3 min and increased at a rate of 5°C min\(^{-1}\) up to 150°C, held 1 min and then increased until 250°C at a rate of 10°C min\(^{-1}\) with a hold time of 7 min. MS operated in electron impact (E.I) mode and data were acquired in selected ion monitoring (SIM) mode. The selected SIM ions and time conditions for each compound are reported in Table S2.

For food samples analyses, oven temperature was maintained at 35°C for 4 min, then raised with a rate of 2.5°C min\(^{-1}\) to 120°C and increased at a rate of 15°C min\(^{-1}\) to 250°C, held for 4 min. Data were acquired in scan, operating in E.I mode with a scan range of 29-400 m/z.

Compounds identification was based on the comparison of their GC retention times and mass spectra with analytical standards and with reference mass spectra from the US National Institute of Standards and Technology (NIST, 2017). Data were analyzed by using MSD ChemStation software (Agilent, Version G1701DA D.01.00).

**Statistical analysis**

For food samples analyses, results were expressed in percentage and were obtained by semi-quantification dividing the peak areas of the analyte of interest by the sum of the peak areas of all the identified compounds. On the other side, in standard samples analyses, results were expressed either as response factors (R.F = analyte peak area / reference compound peak area) or analyte peak areas. The results obtained from each analysis were validated by determining the S.D and the
relative standard deviation (RSD % = 100 x S.D / mean). Results with RSD values ≤ 10% were considered reliable. The student $t$-test was used to evaluate if the differences obtained between the tested penetration distances were statistically reliable. Probability values ≤ 0.05 ($p < 0.05$) were considered statistically significant.
| Articles                                                                 | Stirring speed (rpm) | Temp (°C) | Time (min) | Vial volume (mL) |
|-----------------------------------------------------------------------|----------------------|-----------|------------|-----------------|
| Food Chemistry, Volume 281, 30 May 2019, Pages 49-56                  | 0                    | 37        | 40         | NS              |
| Food Research International, Volume 120, June 2019, Pages 285-294       | 0                    | 50        | 60         | 10              |
| Food Research International, Volume 123, September 2019, Pages 75-87    | 0                    | 55        | 60         | NS              |
| LWT, Volume 112, September 2019, Article 107648                        | 0                    | 80        | 60         | 15              |
| Analytica Chimica Acta, Volume 1081, 12 November 2019, Pages 72-80     | 0                    | 25        | 26         | 4               |
| Food Research International, Volume 123, September 2019, Pages 650-661  | 0                    | 70        | 10         | 20              |
| LWT Volume 11, November 2019, Article 108439                          | 0                    | 60        | 60         | 20              |
| Food Chemistry Volume 285, 1 July 2019, Pages 147-155                  | 0                    | NS        | 2          | NS              |
| Food Chemistry, Volume 275, 1 March 2019, Pages 143-153                | 0                    | 50        | 45         | 15              |
| Biological Control, Volume 133, June 2019, Pages 103-109               | 0                    | 25        | 120        | 500             |
| Food Packaging and Shelf Life, Volume 22, December 2019, Article 100412| 0                    | 60        | 40         | NS              |
| Food Chemistry, Volume 295, 15 October 2019, Pages 72-81               | 0                    | NS        | 15         | 4500            |
| Food Chemistry Volume 283, 15 June 2019, Pages 579-587                 | 0                    | 25        | 45         | 20              |
| Food Chemistry, Volume 282, 1 June 2019, Pages 153-163                 | 0                    | 35        | 20         | 40              |
| Food Research International, Volume 120, June 2019, Pages 92-101        | 80                   | 50        | 45         | 20              |
| Environmental Pollution Volume 249, June 2019, Pages 305-310           | 200                  | 55        | 30         | 75              |
| Microchemical Journal Volume 145, March 2019, Pages 979-987            | 200                  | NS        | 30         | 20              |
| Journal of Agricultural and Food Chemistry 67(49), pp. 13694-13705     | 200                  | 60        | 30         | 20              |
| Food Research International, Volume 121, July 2019, Pages 730-737       | 250                  | 60        | 20         | 20              |
| Food Research International, Volume 123, September 2019, Pages 684-696  | 250                  | 60        | 30         | 20              |
| Food Chemistry, Volume 270, 1 January 2019, Pages 518-526               | 250                  | 45        | 20         | 5               |
| Food Chemistry, Volume 280, 15 May 2019, Pages 83-95                   | 250                  | 60        | 50         | 20              |
| Journal of Chromatography A, In press, corrected proof, Available online 22 October 2019, Article 460647 | 250 | 30 | 30 | NS |
| Analytica Chimica Acta, In press, corrected proof, Available online 20 December 2019 | 250 | 55 | 30 | 20 |
| LWT, Volume 115, November 2019, Article 108425                          | 250                  | 40        | 30         | 20              |
| Food and Chemical Toxicology, Volume 134, December 2019, Article 110829 | 250                  | 50        | 25         | 10              |
| Journal of Chromatography A, In press, corrected proof, Available online 1 October 2019, Article 460584 | 250 | 45 | 50 | 20 |
| Food Chemistry, Volume 287, 30 July 2019, Pages 313-323                 | 250                  | 25        | 10         | 15              |
| Journal of Chromatography A, Volume 1601, 13 September 2019, Pages 60-70 | 250 | 55 | 30 | 20 |
| Food Chemistry, Volume 290, 30 August 2019, Pages 16-23                 | 250                  | 37        | 5          | NS              |
| 31 | Microchemical Journal, Volume 145, March 2019, Pages 942-950 | 250 | 30 | 6 | 10 |
| 32 | Waste Management, Volume 96, 1 August 2019, Pages 1-8 | 250 | 60 | 30 | 20 |
| 33 | Helion, Volume 5, Issue 6, June 2019, Article e01842 | 250 | 60 | 30 | 10 |
| 34 | Journal of Functional Foods, Volume 54, March 2019, Pages 271-280 | 250 | 45 | 120 | NS |
| 35 | LWT, Volume 103, April 2019, Pages 186-191 | 250 | 30 | 40 | 20 |
| 36 | Food Packaging and Shelf Life, Volume 21, September 2019, Article 100371 | 250 | 60 | 20 | 50 |
| 37 | Food Chemistry Volume 27115 January 2019Pages 639-649 | 250 | 45 | 30 | 20 |
| 38 | Food Research International Volume 115January 2019Pages 65-72 | 250 | 40 | 15 | 20 |
| 39 | Food Chemistry Volume 2701 January 2019Pages 344-352 | 250 | 50 | 30 | 20 |
| 40 | International Journal of Food Microbiology, Volume 311, 2 December 2019, Article 108350 | 250 | 50 | 45 | NS |
| 41 | International Dairy Journal, Volume 96, September 2019, Pages 21-28 | 250 | 45 | 45 | 20 |
| 42 | Food Packaging and Shelf Life, Volume 21, September 2019, Article 100328 | 250 | 50 | 30 | 20 |
| 43 | LWT Volume 113, October 2019, Article 108258 | 250 | 60 | 50 | NS |
| 44 | LWT Volume 111, August 2019, Pages 429-435 | 250 | 60 | 50 | NS |
| 45 | Journal of Functional Foods, Volume 52, January 2019, Pages 81-89 | 250 | 60 | 50 | NS |
| 46 | Food Chemistry, Volume 293, 30 September 2019, Pages 8-14 | 250 | 50 | 50 | 20 |
| 47 | Food Chemistry, Volume 291, 1 September 2019, Pages 49-58 | 250 | 60 | 30 | 20 |
| 48 | Science of The Total Environment, Volume 693, 25 November 2019, Article 133635 | 250 | NS | NS | 40 |
| 49 | Foods 8(12),651 | 250 | 40 | 30 | 20 |
| 50 | Journal of Chromatography A, Volume 1603, 11 October 2019, Pages 262-268 | 300 | 40 | 10 | 10 |
| 51 | Food Chemistry, Volume 275, 1 March 2019, Pages 282-291 | 300 | 60 | 45 | 20 |
| 52 | Food Research International, Volume 119, May 2019, Pages 369-377 | 300 | 40 | 30 | NS |
| 53 | Journal of Chromatography A, Volume 1605, 8 November 2019, Article 360341 | 350 | 75 | 55 | 20 |
| 54 | Molecules, 24(24), 4515 | 350 | 50 | 10 | 20 |
| 55 | The International Journal of Biochemistry & Cell Biology, Volume 108, March 2019, Pages 40-50 | 350 | 50 | 30 | NS |
| 56 | LWT, Volume 101, March 2019, Pages 113-122 | 400 | 50 | 60 | 20 |
| 57 | Journal of Agricultural and Food Chemistry 67(47), pp. 13150-13163 | 400 | 45 | 20 | 20 |
| 58 | Food Chemistry, Volume 292, 15 September 2019, Pages 75-80 | 500 | 43 | 45 | 20 |
| 59 | Innovative Food Science & Emerging Technologies, Volume 53, May 2019, Pages 63-69 | 500 | 40 | 30 | 20 |
| 60 | Food and Chemical Toxicology, Volume 130, August 2019, Pages 61-67 | 500 | 70 | 20 | 20 |
| 61 | Talanta, Volume 191, 1 January 2019, Pages 535-544 | 500 | 30/60 | 60 | 20 |
| 62 | Innovative Food Science & Emerging Technologies, Volume 56, August 2019, Article 102177 | 500 | 60 | 5 | 20 |
| 63 | Food Research International, Volume 120, June 2019, Pages 514-522 | 500 | 30 | 40 | 20 |
|   | Title                                                                 | Volume  | Pages/Issue | Issue Dates          | Pages/Issue |
|---|---------------------------------------------------------------|--------|------------|----------------------|-------------|
| 64 | Food and Chemical Toxicology, Volume 132, October 2019, Article 110647 |        |            |                      | 500         |
| 65 | Food Chemistry, Volume 285, 1 July 2019, Pages 39-45          |        |            |                      | 500         |
| 66 | Microchemical Journal, Volume 150, November 2019, Article 104094 |        |            |                      | 500         |
| 67 | Food Research International, Volume 119, May 2019, Pages 733-740|        |            |                      | 500         |
| 68 | Food Research International, Volume 125, November 2019, Article 108548 |        |            |                      | 500         |
| 69 | Food Research International, Volume 123, September 2019, Pages 722-731 |        |            |                      | 500         |
| 70 | Food Chemistry Volume 27415, February 2019, Pages 39-45       |        |            |                      | 500         |
| 71 | International Journal of Refrigeration Vol Volume 106, October 2019, Pages 24-32 |        |            |                      | 500         |
| 72 | Innovative Food Science & Emerging Technologies, Volume 58, December 2019, Article 102213 |        |            |                      | 500         |
| 73 | Food Research International, Volume 119, May 2019, Pages 554-563 |        |            |                      | 500         |
| 74 | Journal of Dairy Science, Volume 102, Issue 1, January 2019, Pages 202-210 |        |            |                      | 500         |
| 75 | Food Research International, Volume 122, August 2019, Pages 56-65 |        |            |                      | 500         |
| 76 | Journal of Food Engineering, Volume 260, November 2019, Pages 22-29 |        |            |                      | 500         |
| 77 | Innovative Food Science & Emerging Technologies, Volume 54, June 2019, Pages 64-77 |        |            |                      | 500         |
| 78 | LWT Volume 111, August 2019, Pages 1-8                         |        |            |                      | 500         |
| 79 | Journal of Agricultural and Food Chemistry 67(49), pp. 13420-13429 |        |            |                      | 500         |
| 80 | Separations, 6(4),46                                          |        |            |                      | 500         |
| 81 | Food Control, Volume 100, June 2019, Pages 335-349            |        |            |                      | 500         |
| 82 | Journal of Chromatography A, Volume 1588, 15 March 2019, Pages 17-24 |        |            |                      | 600         |
| 83 | Atlanta, Volume 200, 1 August 2019, Pages 415-423             |        |            |                      | 600         |
| 84 | LWT, Volume 109, July 2019, Pages 83-92                       |        |            |                      | 600         |
| 85 | Scientia Horticulture Volume 25227, June 2019, Pages 121-129  |        |            |                      | 600         |
| 86 | Food Research International, Volume 125, November 2019, Article 108568 |        |            |                      | 600         |
| 87 | Journal of Chromatography A, Volume 1592, 10 May 2019, Pages 9-18 |        |            |                      | 700         |
| 88 | Food Chemistry Volume 301, 15 December 2019, Article 125252    |        |            |                      | 700         |
| 89 | Analytica Chimica Acta, In press, corrected proof, Available online 3 December 2019 |        |            |                      | 750         |
| 90 | Microchemical Journal, In press, corrected proof, Available online 29 November 2019, Article 104459 |        |            |                      | 750         |
| 91 | Journal of Chromatography B, Volume 1133, 1 December 2019, Article 121824 |        |            |                      | 750         |
| 92 | Journal of Chromatography A, Volume 1591, 26 April 2019, Pages 55-61 |        |            |                      | 750         |
| 93 | Polymer Testing, Volume 73, February 2019, Pages 94-103        |        |            |                      | 800         |
| 94 | Food Chemistry, Volume 291, 1 September 2019, Pages 187-198    |        |            |                      | 1000        |
| 95 | Journal of Chromatography A, Volume 1603, 11 October 2019, Pages 92-101 | 1000 | 35 | 45 | NS |
| 96 | Journal of Chromatography A, Volume 1602, 27 September 2019, Pages 142-149 | 1000 | 25 | 30 | 20 |
| 97 | Arabian Journal of Chemistry, Volume 12, Issue 8, December 2019, Pages 1934-1944 | 1275 | 25 | 30 | NS |
| 98 | Food Chemistry, Volume 301, 15 December 2019, Article 125264 | NS | 70 | 30 | NS |
| 99 | Industrial Crops and Products, Volume 127, January 2019, Pages 225-231 | NS | 45 | 5 | 40 |
| 100 | Food Chemistry, Volume 272, 30 January 2019, Pages 723-731 | NS | 60 | 40 | 20 |
| 101 | Microchemical Journal, Volume 149, September 2019, Article 103991 | NS | 20 | 15 | 20 |
| 102 | Microchemical Journal, Volume 148, July 2019, Pages 643-651 | NS | 50 | 30 | 15 |
| 103 | LWT, Volume 104, May 2019, Pages 38-44 | NS | 40 | 55 | 20 |
| 104 | Food Chemistry, Volume 277, 30 March 2019, Pages 753-765 | NS | 35 | 25 | 20 |
| 105 | Meat Science, Volume 151, May 2019, Pages 43-53 | NS | 40 | 45 | 20 |
| 106 | LWT, Volume 102, March 2019, Pages 304-309 | NS | 50 | 50 | 20 |
| 107 | LWT, Volume 112, September 2019, Article 108256 | NS | 40 | 30 | 20 |
| 108 | Food Chemistry, Volume 283, 15 June 2019, Pages 566-578 | NS | 30 | 75 | 90 |
| 109 | Food Research International, Volume 121, July 2019, Pages 765-775 | NS | 40 | 70 | 20 |
| 110 | Food Research International, Volume 119, May 2019, Pages 23-33 | NS | 60 | 80 | 15 |
| 111 | Food Research International, Volume 125, November 2019, Article 108611 | NS | 60 | 50 | 15 |
| 112 | LWT, Volume 112, September 2019, Article 108264 | NS | 45 | 30 | 15 |
| 113 | LWT, Volume 108, July 2019, Pages 268-276 | NS | 40 | 40 | 20 |
| 114 | LWT, Volume 99, January 2019, Pages 328-345 | NS | 80 | 30 | 20 |
| 115 | Journal of Chromatography A, Volume 1599, 16 August 2019, Pages 17-24 | NS | 75 | 15 | 10 |
| 116 | Food Research International, Volume 123, September 2019, Pages 550-558 | NS | 80 | 70 | 20 |
| 117 | LWT, Volume 108, July 2019, Pages 221-232 | NS | 80 | 30 | 20 |
| 118 | Food Chemistry, Volume 293, 30 September 2019, Pages 151-160 | NS | 45 | 30 | 20 |
| 119 | Food Research International, Volume 116, February 2019, Pages 767-777 | NS | 38 | 60 | 100 |
| 120 | Scientia Horticulturae, Volume 250, 10 May 2019, Pages 207-213 | NS | 25 | 40 | 20 |
| 121 | Microchemical Journal, Volume 149, September 2019, Article 104064 | NS | 60 | 15 | 20 |
| 122 | Analytical Biochemistry, Volume 578, 1 August 2019, Pages 36-44 | NS | 37 | 50 | 20 |
| 123 | Journal of Functional Foods, Volume 59, August 2019, Pages 261-271 | NS | 40 | 35 | 10 |
| 124 | Microchemical Journal, Volume 146, May 2019, Pages 1026-1032 | NS | 35 | 20 | 15 |
| 125 | Food Research International, Volume 119, May 2019, Pages 84-98 | NS | 60 | 35 | 20 |
| 126 | Food Research International, Volume 123, September 2019, Pages 481-502 | NS | 75 | 50 | 20 |
| 127 | Flora, Volume 258, September 2019, Article 151428 | NS | 25 | 50 | 10 |
| 128 | Atlanta, Volume 192, 15 January 2019, Pages 486-491 | NS | 60 | 30 | 10 |
| 129 | Atlanta, Volume 202, 1 September 2019, Pages 90-95 | NS | 60 | 30 | 20 |
| 130 | Microchemical Journal, Volume 146, May 2019, Pages 986-996 | NS | 60 | 65 | 100 |
| 131 | Journal of Chromatography A, Volume 1594, 7 June 2019, Pages 45-53 | NS | 70 | 20 | 15 |
| 132 | Food Research International, Volume 120, June 2019, Pages 620-630 | NS | 60 | 60 | 15 |
| 133 | Journal of Plant Physiology, Volume 240, September 2019, Article 152994 | NS | 45 | 20 | 20 |
| 134 | Microchemical Journal, In press, corrected proof, Available online 16 December 2019, Article 104532 | NS | NS | NS | 20 |
| 135 | Science of The Total Environment, Volume 669, 15 June 2019, Pages 160-167 | NS | 70 | 60 | 10 |
| 136 | Food Research International, Volume 119, May 2019, Pages 196-206 | NS | 60 | 50 | 10 |
| 137 | Food Chemistry, Volume 278, 25 April 2019, Pages 406-414 | NS | 40 | 60 | 20 |
| 138 | Journal of Chromatography A, Volume 1607, 6 December 2019, Article 460398 | NS | 100 | 25 | 22 |
| 139 | Food Research International, Volume 125, November 2019, Article 108625 | NS | 40 | 60 | 20 |
| 140 | Crop Protection, Volume 124, October 2019, Article 104839 | NS | 60 | 35 | 10 |
| 141 | Food Chemistry, Volume 285, 1 July 2019, Pages 347-354 | NS | 30 | 60 | N. S |
| 142 | Scientia Horticulturae, Volume 244, 26 January 2019, Pages 257-262 | NS | 60 | 105 | 20 |
| 143 | Science of The Total Environment, Volume 681, 1 September 2019, Pages 392-399 | NS | 60 | 50 | 20 |
| 144 | Atlanta, Volume 198, 1 June 2019, Pages 193-199 | NS | 45 | 15 | 10 |
| 145 | Analytica Chimica Acta, Volume 1047, 24 January 2019, Pages 1-8 | NS | NS | NS | 20 |
| 146 | International Journal of Food Microbiology, Volume 292, 2 March 2019, Pages 83-90 | NS | 60 | 60 | 20 |
| 147 | Postharvest Biology and Technology, Volume 152, June 2019, Pages 127-138 | NS | 40 | 40 | 10 |
| 148 | Talanta, Volume 205, 1 December 2019, Article 120080 | NS | 45 | 15 | N. S |
| 149 | Food Research International Volume 122August 2019Pages 10-15 | NS | 50 | 30 | 20 |
| 150 | Safety and Health at Work Volume 10, Issue 1March 2019Pages 114-121 | NS | 110 | 3 | 20 |
| 151 | Journal of Bioscience and Bioengineering Volume 127, Issue 6June 2019Pages 710-713 | NS | 35 | 40 | 20 |
| 152 | Food Research International Volume 120June 2019Pages 83-91 | NS | 45 | 45 | 20 |
| 153 | Food Chemistry Volume 27415 February 2019Pages 118-122 | NS | 50 | 35 | 15 |
| 154 | LWT Volume 113October 2019Article 108326 | NS | 37 | NS | 10 |
| 155 | Food Chemistry Volume 27230 January 2019Pages 39-48 | NS | 60 | 50 | 20 |
| 156 | International Journal of Food Microbiology Volume 3112 December 2019Article 108314 | NS | 40 | 20 | 20 |
| 157 | Food Bioscience Volume 27February 2019Pages 30-36 | NS | 55 | 55 | 15 |
| 158 | LWT Volume 108July 2019Pages 400-406 | NS | 50 | 70 | 20 |
| 159 | Food Quality and Preference Volume 78December 2019Article 103735 | NS | 40 | 25 | 20 |
| 160 | Food Chemistry Volume 28, 915 August 2019Pages 340-350 | NS | 60 | 70 | 15 |
| 161 | Food Chemistry, Volume 279, 1 May 2019, Pages 356-363 | NS | RT | 60 | 15 |
| 162 | Journal of Environmental Management, Volume 249, 1 November 2019, Article 109426 | NS | 70 | 15 | 15 |
| 163 | Journal of Chromatography A, In press, corrected proof Available online 26 November 2019, Article 460739 | NS | 50 | 40 | 20 |
| 164 | Food and Chemical Toxicology Volume 134, December 2019, Article 110833 | NS | 60 | 40 | 20 |
| 165 | Food Research International, Volume 125, November 2019, Article 108531 | NS | 50 | 60 | 15 |
| 166 | International Journal of Food Microbiology, Volume 290, 2 February 2019, Pages 86-95 | NS | 40 | 25 | 20 |
| 167 | LWT Volume 108, July 2019, Pages 214-220 | NS | 45 | 45 | 15 |
| 168 | Food Chemistry Volume 276, 15 March 2019, Pages 572-582 | NS | 80 | 23 | 20 |
| 169 | Postharvest Biology and Technology, Volume 154, August 2019, Pages 11-20 | NS | 40 | 60 | 20 |
| 170 | Plant Science, Volume 287, October 2019, Article 110187 | NS | 50 | 30 | 20 |
| 171 | Food Research International, Volume 119, May 2019, Pages 152-160 | NS | 50 | 60 | 20 |
| 172 | Food Chemistry, Volume 287, 30 July 2019, Pages 186-196 | NS | 40 | 60 | 250 |
| 173 | Journal of Cereal Science, Volume 85, January 2019, Pages 6-14 | NS | 60 | 60 | 20 |
| 174 | Food Chemistry, Volume 289, 15 August 2019, Pages 215-222 | NS | 45 | 50 | 20 |
| 175 | Food Chemistry, Volume 290, 30 August 2019, Pages 135-143 | NS | 60 | 55 | 15 |
| 176 | Reproductive Toxicology, Volume 84, March 2019, Pages 114-121 | NS | NS | NS | 20 |
| 177 | Food Research International, Volume 121, July 2019, Pages 593-603 | NS | 50 | 45 | 15 |
| 178 | Journal of Chromatography A, Volume 1597, 19 July 2019, Pages 132-141 | NS | 50 | 30 | 20 |
| 179 | Food Research International, Volume 122, August 2019, Pages 318-329 | NS | 45 | 40 | 20 |
| 180 | Food Chemistry, Volume 289, 15 August 2019, Pages 645-656 | NS | 40 | 60 | 15 |
| 181 | Heliyon Volume 5, Issue 6, June 2019, Article e01953 | NS | 60 | 30 | 20 |
| 182 | LWT, Volume 104, May 2019, Pages 8-15 | NS | 60 | 30 | NS |
| 183 | LWT, Volume 111, August 2019, Pages 211-217 | NS | 40 | 60 | NS |
| 184 | Journal of Food Engineering, Volume 259, October 2019, Pages 12-20 | NS | 40 | 30 | NS |
| 185 | Food Chemistry, Volume 286, 15 July 2019, Pages 659-668 | NS | 45 | 20 | 20 |
| 186 | International Journal of Food Microbiology, Volume 299, 16 June 2019, Pages 8-22 | NS | 37 | 50 | 40 |
| 187 | Microchemical Journal, Volume 145, March 2019, Pages 1119-1128 | NS | 60 | 60 | 20 |
| 188 | Food Chemistry, Volume 277, 30 March 2019, Pages 84-95 | NS | 50 | 60 | 120 |
| 189 | The Journal of Supercritical Fluids, Volume 143, January 2019, Pages 211-222 | NS | 50 | 10 | 22 |
| 190 | Food Chemistry, Volume 271, 15 January 2019, Pages 298-308 | NS | 60 | 30 | 10 |
| 191 | LWT, Volume 101, March 2019, Pages 145-151 | NS | 50 | 60 | 100 |
| 192 | Food Microbiology, Volume 77, February 2019, Pages 166-172 | NS | 40 | 30 | 20 |
| 193 | Postharvest Biology and Technology, Volume 153, July 2019, Pages 110187 | NS | 50 | 60 | 10 |
| 194 | Food Chemistry, Volume 292, 15 September 2019, Pages 227-236 | NS | 60 | 30 | 15 |
| 195 | Biological Control, Volume 129, February 2019, Pages 195-200 | NS | NS | NS | 15 |
Table S2. Experimental conditions used in GC-MS analyses. Time windows and selected ions for each monitored compound in selected ion monitoring mode (SIM).

* VOCs: Volatile organic compounds.

| Groups                        | Compounds         | Time windows (min) | SIM Ions (m/z) |
|-------------------------------|-------------------|--------------------|----------------|
| **Study on Free fatty acids** |                   |                    |                |
| 1                             | Butanoic acid     | 13 – 24.5          | 73; 88         |
| 2                             | Isovaleric acid   | 24.5 – 27          | 60; 87         |
| 3                             | Hexanoic acid     | 27 – 29            | 73; 87         |
| 4                             | Octanoic acid     | 29 – 32            | 101; 115       |
| 5                             | Decanoic acid     | 32 – 40            | 129; 172       |
| **Study on mixtures of 6 VOCs* standards** | | | |
| 1                             | 3-Methylbutanal   | 0 – 13             | 44; 58         |
| 2                             | Hexen-1-ol        | 13 – 23.3          | 67; 82         |
| 3                             | Furfural          | 23.3 – 24.5        | 96; 95         |
| 4                             | Furfuryl acetate  | 24.5 – 24.8        | 98; 140        |
| 5                             | Linalool          | 24.8 – 28.1        | 71; 93         |
| 6                             | Guaiacol          | 28.1 – 30.1        | 109; 124       |
**Table S3.** Analyses of “primo fiore” wine samples: percentage (%) of each identified volatile organic compound (VOC) obtained at two fiber exposition depths (20 and 40 mm) at different temperatures (30, 50 and 80°C). Values are expressed as mean ± standard deviation. % = 100 x peak area analyte / total peak area. *: Differences were statistically significant for the VOCs considered ($p \leq 0.05$).

| VOCs                        | 30°C  | 50°C  | 80°C  |
|-----------------------------|-------|-------|-------|
|                             | 20 mm | 40 mm | 20 mm | 40 mm | 20 mm | 40 mm |
| Ethyl acetate               | 12.4 ± 0.4 | 8.4 ± 0.08* | 8.2 ± 0.2 | 5.8 ± 0.07* | 8.0 ± 0.7 | 5.8 ± 0.7 |
| Ethanol                     | 53.2 ± 4.1 | 37.9 ± 0.5* | 53.4 ± 0.6 | 43.7 ± 0.1* | 58.9 ± 0.2 | 52.1 ± 0.16* |
| Ethyl butanoate             | 1.0 ± 0.05 | 1.8 ± 0.1* | 1.3 ± 0.03 | 1.3 ± 0.01 | 0.7 ± 0.1 | 0.6 ± 0.2 |
| 1-Propanol, 2 methyl        | 0.8 ± 0.01 | 0.8 ± 0.01 | 1.0 ± 0.02 | 0.8 ± 0.01* | 0.8 ± 0.1 | 0.7 ± 0.02 |
| Isoamyl acetate             | 5.1 ± 0.2 | 11.1 ± 0.01* | 4.7 ± 0.5 | 4.0 ± 0.01 | 2.5 ± 0.03 | 1.9 ± 0.02* |
| 1-butanol, 3-methyl         | 9.6 ± 0.3 | 11.0 ± 0.01* | 10.8 ± 1.0 | 10.2 ± 0.01 | 8.6 ± 0.5 | 8.4 ± 0.4 |
| Ethyl caproate              | 8.8 ± 0.6 | 10.0 ± 0.01 | 6.9 ± 0.3 | 9.6 ± 0.01* | 4.7 ± 0.2 | 4.1 ± 0.2 |
| Hexyl acetate               | 0.6 ± 0.03 | 1.4 ± 0.01* | 0.3 ± 0.1 | 1.1 ± 0.00* | 0.2 ± 0.02 | 0.2 ± 0.03 |
| Ethyl lactate               | 0.5 ± 0.03 | 1.6 ± 0.02* | 1.2 ± 0.02 | 1.5 ± 0.00* | 1.7 ± 0.04 | 1.5 ± 0.03* |
| 1-Hexanol                   | 0.3 ± 0.02 | 1.1 ± 0.02* | 0.5 ± 0.01 | 1.1 ± 0.00* | 0.8 ± 0.02 | 0.6 ± 0.01* |
| Ethyl octanoate             | 7.4 ± 0.6 | 7.4 ± 0.00 | 5.7 ± 0.3 | 6.5 ± 0.00 | 2.4 ± 0.3 | 5.0 ± 0.2* |
| Acetic acid                 | -     | 0.3 ± 0.00* | 0.2 ± 0.05 | 0.3 ± 0.01 | 0.6 ± 0.06 | 0.5 ± 0.03 |
| Ethyl decanoate             | 1.3 ± 0.2 | 1.6 ± 0.01 | 1.0 ± 0.03 | 1.5 ± 0.00* | 0.3 ± 0.02 | 0.7 ± 0.07* |
| Ethyl succinate             | 0.2 ± 0.02 | 0.6 ± 0.00* | 0.5 ± 0.01 | 1.2 ± 0.00* | 1.0 ± 0.07 | 1.6 ± 0.04* |
| Ethyl decenoate             | 0.06 ± 0.01 | 0.1 ± 0.01* | 0.07 ± 0.00 | 0.1 ± 0.00* | 0.2 ± 0.04 | 0.2 ± 0.03 |
| Acetic acid, 2-phenylethyl ester | 0.05 ± 0.00 | 0.1 ± 0.00* | 0.1 ± 0.01 | 0.4 ± 0.01* | 0.2 ± 0.01 | 0.7 ± 0.1* |
| Hexanoic acid               | 1.9 ± 0.1 | 1.3 ± 0.4 | 0.6 ± 0.01 | 2.8 ± 0.2* | 1.4 ± 0.01 | 2.3 ± 0.4 |
| Phenylethyl alcohol         | 0.6 ± 0.04 | 1.1 ± 0.03* | 0.9 ± 0.01 | 1.5 ± 0.01* | 1.4 ± 0.1 | 1.9 ± 0.03* |
| Octanoic acid               | 0.6 ± 0.02 | 1.9 ± 0.2* | 1.9 ± 0.2 | 4.6 ± 0.02* | 4.4 ± 0.3 | 7.5 ± 0.2* |
| Decanoic acid               | 0.06 ± 0.00 | 0.5 ± 0.1* | 0.5 ± 0.07 | 2.0 ± 0.02* | 1.2 ± 0.1 | 3.4 ± 0.07* |

Sum of peak areas of identified VOCs (x 10^6): 1452 ± 25 | 1929 ± 3* | 1699 ± 64 | 1984 ± 2* | 1726 ± 32 | 1855 ± 15*
**Table S4.** Analyses of “Tavernello” wine samples: percentage (%) of each identified volatile organic compound (VOC) obtained at two fiber exposition depths (20 and 40 mm) after 20 min at 35°C. Values are expressed as mean ± standard deviation. % = 100 x peak area analyte / total peak area. *: Differences were statistically significant for the VOCs considered (p ≤ 0.05).

|                | 20mm            | 40mm            |
|----------------|-----------------|-----------------|
|                | Mean± std dev (%) | Mean± std dev (%) |
| Ethanol        | 91.66 ± 0.05    | 91.29 ± 0.01*   |
| 3-Methyl-1-butanol | 6.01 ± 0.04    | 6.40 ± 0.05*    |
| Ethyl butyrate | 0.10 ± 0.00     | 0.11 ± 0.00*    |
| Isoamyl acetate | 1.92 ± 0.00    | 1.86 ± 0.05     |
| Gamma-butyrolactone | 0.05 ± 0.00    | 0.08 ± 0.01*    |
| Hexyl acetate  | 0.07 ± 0.00     | 0.07 ± 0.00     |
| Ethyl octanoate | 0.18 ± 0.00    | 0.18 ± 0.00     |
| Ethyl decanoate | 0.00 ± 0.00    | 0.01 ± 0.00*    |
| Sum of peak areas of identified VOCs | 602 ± 22 x 10^6 | 777 ± 15 x 10^6* |

**Table S5.** Analyses of caciocavallo cheese. Percentage (%) of each identified volatile organic compound (VOC) obtained at two fiber exposition depths (20 and 40 mm) after 30 min of extraction at 45°C. Values are expressed as mean ± standard deviation (std dev). % = 100 x peak area analyte / total peak area. *: Differences were statistically significant for the VOCs considered (p ≤ 0.05).

|                | 20mm            | 40mm            |
|----------------|-----------------|-----------------|
|                | Mean± std dev (%) | Mean± std dev (%) |
| 2-Heptanone    | 0.50 ± 0.02     | 0.76 ± 0.06*    |
| D-Limonene     | 0.52 ± 0.01     | 0.89 ± 0.02*    |
| 3-Methyl-1-butanol | 0.15 ± 0.02    | 0.19 ± 0.03    |
| Acetoin        | 2.16 ± 0.17     | 5.60 ± 0.28*    |
| 2-propanone, 1-hydroxy | 0.05 ± 0.00    | 0.13 ± 0.00*    |
| Acetic acid    | 0.08 ± 0.00     | 4.69 ± 0.55*    |
| Benzaldehyde   | 0.17 ± 0.00     | 0.23 ± 0.00*    |
| Butanoic acid  | 59.93 ± 2.15    | 46.72 ± 0.11*   |
| Isovaleric acid   | 0.54 ± 0.00 | 1.27 ± 0.06* |
|------------------|-------------|--------------|
| Pentanoic acid   | 1.06 ± 0.07 | 2.76 ± 0.15* |
| Hexanoic acid    | 32.91 ± 2.12 | 33.32 ± 0.54 |
| Octanoic acid    | 1.93 ± 0.13 | 3.44 ± 0.27* |

| Sum of peak areas of identified VOCs | 245 ±14 x 10^6 | 476±17 x 10^6* |

**Table S6.** Analyses of tea samples. Percentage (%) of each identified volatile organic compound (VOC) obtained at two fiber exposition depths (20 and 40 mm) after 40 min of extraction at 50°C. Values are expressed as mean ± standard deviation (std dev). % = 100 x peak area analyte / total peak area. *: Differences were statistically significant for the VOCs considered (p ≤ 0.05).

|                     | 20 mm     | 40 mm     |
|---------------------|-----------|-----------|
|                     | Mean ± std dev (%) | Mean ± std dev (%) |
| 2-Methylbutanal     | 4.5 ± 0.3 | 4.0 ± 0.3 |
| Pentanal            | 3.1 ± 0.3 | 3.2 ± 0.3 |
| 2-Ethylfuran        | 2.6 ± 0.4 | 2.9 ± 0.3 |
| 2-Pentenal          | 1.8 ± 0.3 | 1.5 ± 0.2 |
| Hexanal             | 24.2 ± 2.3 | 35.5 ± 1.6* |
| Furfural            | 2.6 ± 0.4 | 2.5 ± 0.3 |
| 2-Hexenal           | 29.8 ± 3.2 | 26.6 ± 0.8 |
| Heptanal            | 2.6 ± 0.4 | 2.2 ± 0.3 |
| 2-Heptenal          | 6.5 ± 1.2 | 4.2 ± 0.8 |
| Benzaldehyde        | 11.4 ± 1.8 | 8.4 ± 0.6 |
| 6-Methylhept-5-en-2-one | 4.3 ± 0.8 | 3.0 ± 0.5 |
| 2,4-Heptadienal     | 6.6 ± 0.7 | 5.7 ± 0.3 |

| Sum of peak areas of identified VOCs | 19.5 ± 0.4 x 10^6 | 22.7 ± 0.9 x 10^6* |
**Table S7.** Analyses of chicken. Percentage (%) of each identified volatile organic compound (VOC) obtained at two fiber exposition depths (20 and 40 mm) after 30 min of extraction at 40°C. Values are expressed as mean ± standard deviation (std dev). % = 100 x peak area analyte / total peak area. *: Differences were statistically significant for the VOCs considered (p ≤ 0.05).

|                | 20 mm Mean ± std dev (%) | 40 mm Mean ± std dev (%) |
|----------------|--------------------------|--------------------------|
| 2-Methyl-1-propanol | 2.3 ± 0.6                | 1.52 ± 0.14               |
| Nonane          | 0.5 ± 0.01               | 1.35 ± 0.10*              |
| Heptanone       | 0.6 ± 0.03               | 0.94 ± 0.20               |
| 3-methyl-1-butanol | 25.3 ± 5.4             | 36.50 ± 1.19              |
| Acetoin         | 33.5 ± 4.2               | 18.40 ± 1.95*             |
| Nonanone        | 0.8 ± 0.2                | 1.15 ± 0.06               |
| Leucicacid      | 6.15 ± 0.2               | 15.18 ± 1.85*             |
| 2-ethyl-1-Hexanol | 1.15 ± 0.02             | 1.01 ± 0.07               |
| Phenylehylalcohol | 8.22 ± 1.77             | 8.30 ± 0.51               |
| Phenol          | 21.53 ± 0.07             | 13.31 ± 0.30*             |
| Sum of peak areas of identified VOCs | 1328 ± 5 x 10^5 | 2550 ± 2 x 10^5* |
Figure S1.

Figure S1. Analyses of a mixture of 6 volatile organic compounds (VOCs). Peak area of each VOC obtained at two fiber exposition depths (20 and 40 mm) at various temperatures of extraction (40, 60 and 80 °C). *: data were significant for p < 0.05.
In a study performed on a mixture of VOCs, the RF differences was statistically significant for all 5 compounds at 250 rpm. With the increase of the stirring speed, the variations were reduced, as expected, but remained statistically significant for some analytes (Figure S2).
It is important to note that the aims of this study were neither to determine the best stirring rate for HS-SPME experiments, nor the right sample-fiber distance. Our aim was simply to demonstrate that in pre-equilibrium conditions, as for several published papers, it is important to specify the sample-fiber distance or the fiber penetration depth in order to increase the reproducibility of the researches reported in literature.

In addition, few researchers have started very recently to take into consideration this parameter, giving info in their papers about the distance between the fiber tip and the sample surface or the fiber penetration depths (Food Research International, Volume 123, September 2019, Pages 650-661; Food Packaging and Shelf Life, Volume 22, December 2019, Article 100412; Food Chemistry, Volume 292, 15 September 2019, Pages 227-236).