*Supporting Information of*

# Resolving coffee roasting-degree phases based on the analysis of volatile compounds in the roasting off-gas by photoionization time-of-flight mass spectrometry (PI-TOFMS) and statistical data analysis: Towards a PI-TOFMS roasting model

Hendryk Czech[†], Claudia Schepler[†], Sophie Klingbeil[†,§], Sven Ehlert[†,#], Jessalin Howell[&], Ralf Zimmermann[†,§,‖,*]

[†]*Joint Mass Spectrometry Center, Chair of Analytical Chemistry, Institute of Chemistry, University of Rostock, 18059 Rostock, Germany*

[§]*Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) - www.hice-vi.eu*

[#]*Photonion GmbH, 19061 Schwerin, Germany*

[&]*The J.M. Smucker Company, 1 Strawberry Lane, Orrville, Ohio 44667, USA*

[‖]*Joint Mass Spectrometry Center, Cooperation Group "Comprehensive Molecular Analytics", Institute of Ecological Chemistry, Helmholtz Zentrum München – German Research Center for Environmental Health, 85764 Neuherberg, Germany*

**Corresponding Author**

*E-mail: ralf.zimmermann@helmholtz-muenchen.de, ralf.zimmermann@uni-rostock.de. Phone: +49 (0)381 498 - 6460.

Fax: +49 (0) 381 498 - 118 6527.

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Table S1 Resulting pairs of m/z with highest Fisher ratio

Table S2 Molecular assignments for pairs of m/z in Table S1

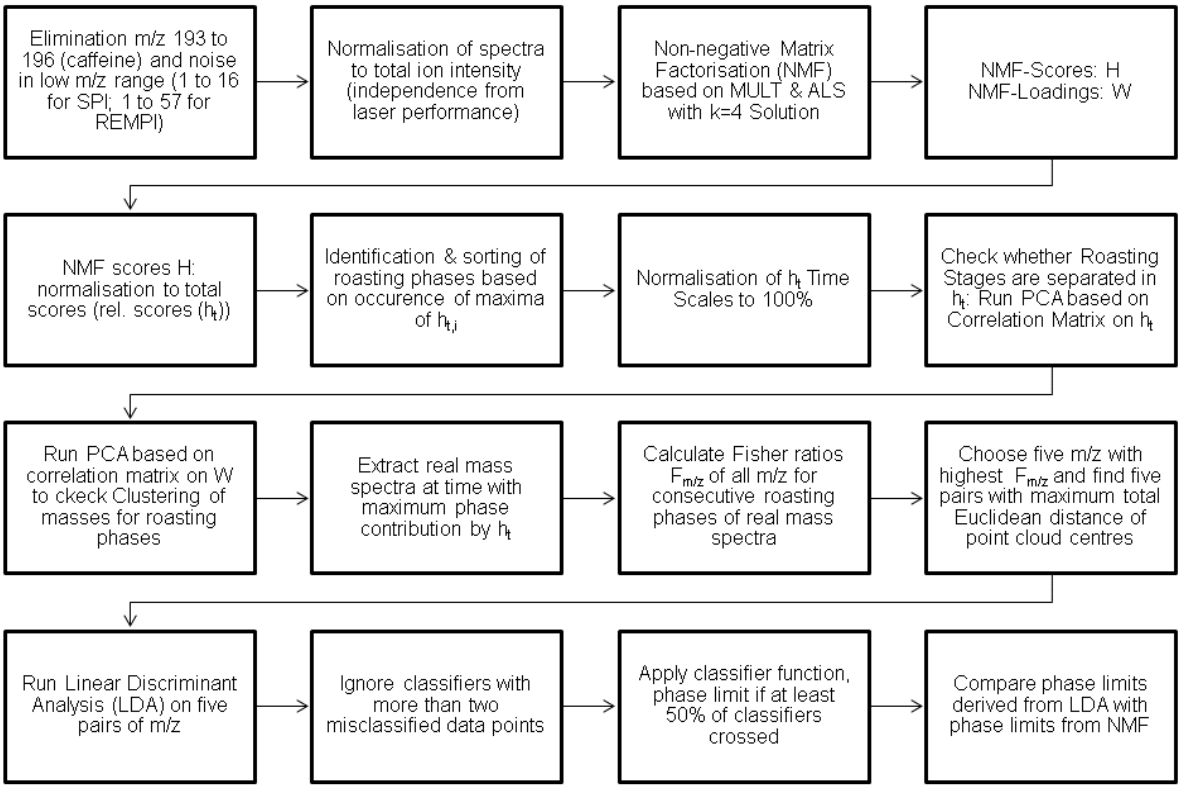


**Fig. S1** Flow chart of data treatment and statistics.

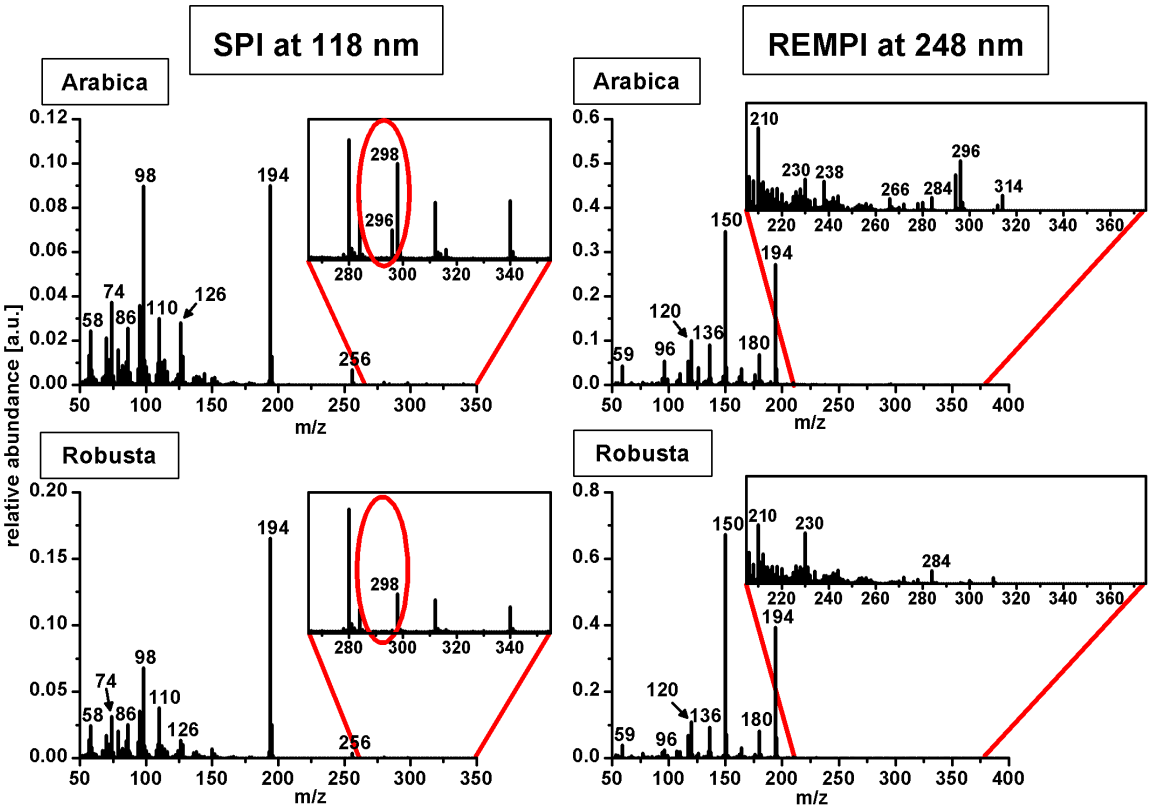


**Fig. S2** Mass spectra of fast roast experiments (SPI at 118 nm (average of three experiments in each case from 400 to 600 s) and REMPI at 248 nm (average of three experiments in each case over the whole roasting time)) for the two cultivars.

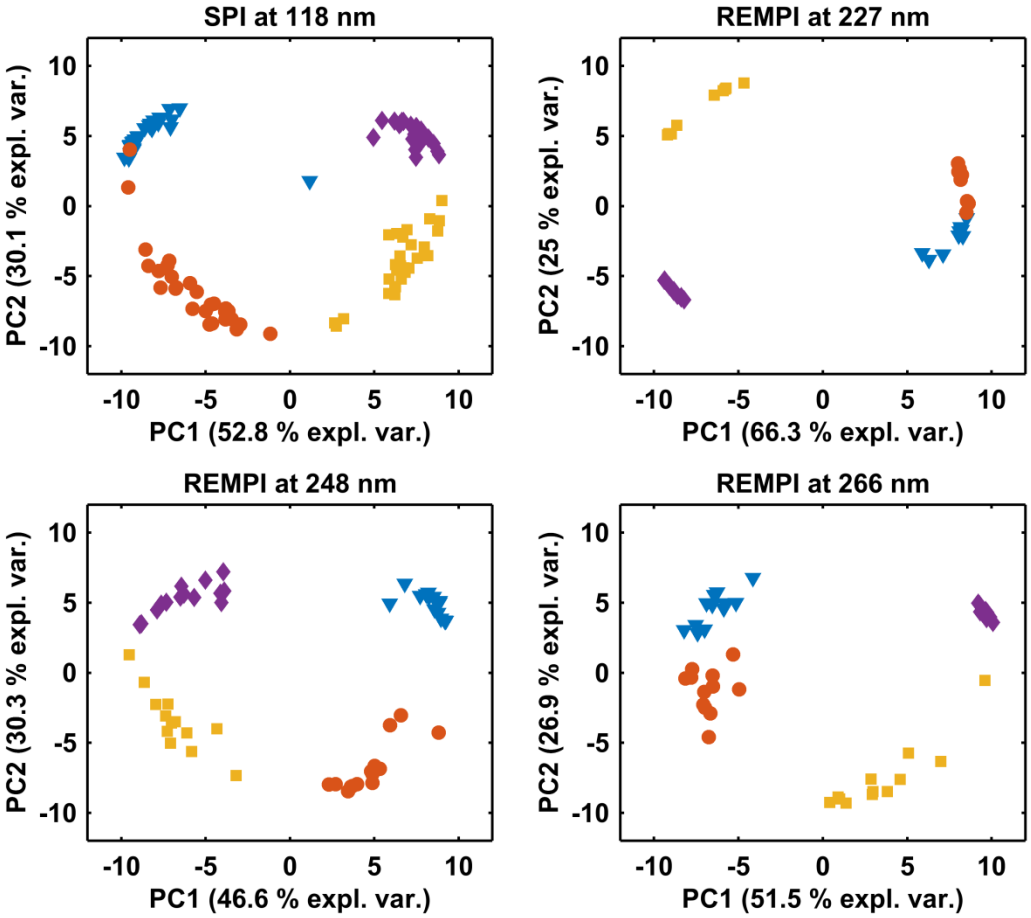


**Fig. S3** PCA-scores of time-normalized roasting phases derived from relative NMF scores $h_t$. Clustering of the roasting phases ‘evaporation‘ (blue triangle), ‘early roast’ (red circle), ‘late roast’ (yellow square) and ‘overroast’ (purple diamond) appears in every scatter plot, however the separation performance between different roasting phases varies at photoionisation wavelengths.

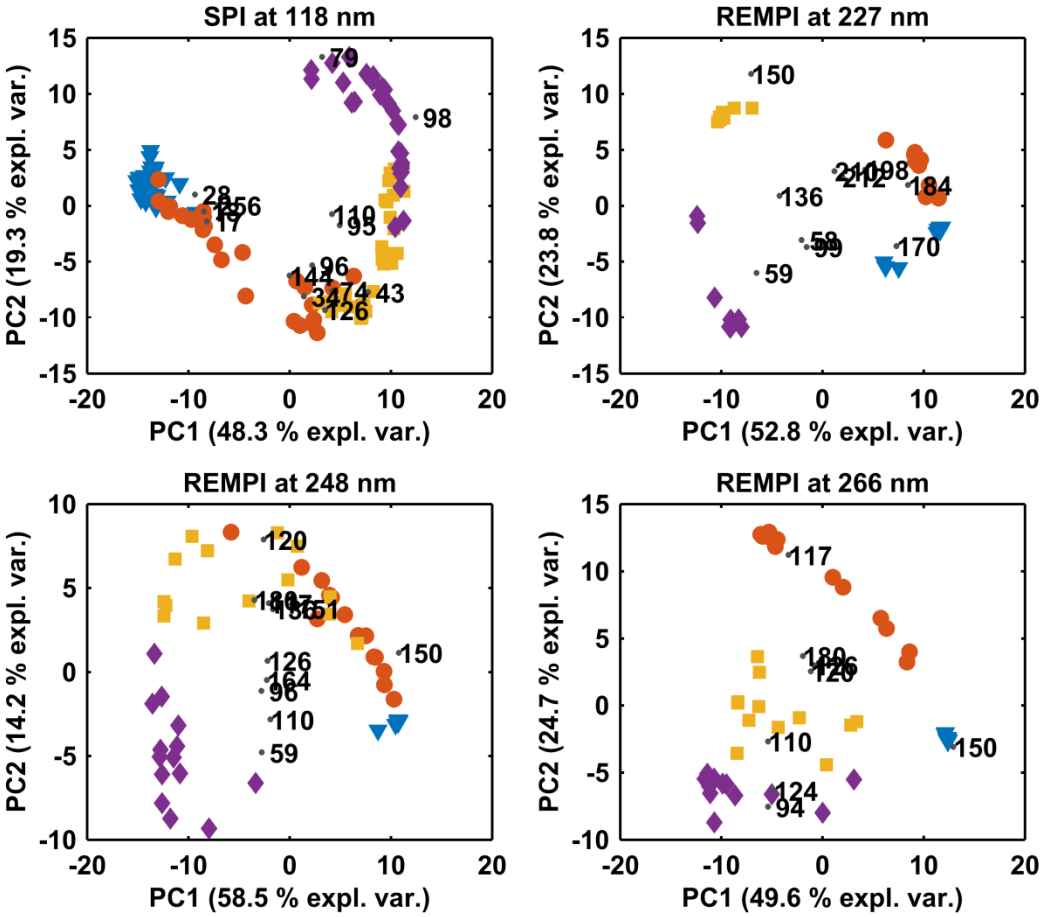


**Fig. S4** PCA-biplots of NMF factor loadings W. Phase separation does not appear as clear as for relative NMF score $h_t$ (Fig. S5). However, for SPI known indicators such as pyridine (m/z 79) for 'overroast' or hexadecanoic acid (m/z 256) and water (m/z 18) for 'evaporation' were correctly assigned. Additionally, for REMPI at 266 nm PCA-biplot looks similar to results of Dorfner et al.[1] For an appropriate visualization, only the most relevant m/z are depicted.

**Table S1.** Resulting m/z with highest Fisher ratio arranged to pairs with maximum total Euclidean distance. Tentative assignments of molecular structures can be found in Table S2.

| | SPI at 118 nm | | REMPI at 227 nm | | REMPI at 248 nm | | REMPI at 266 nm | |
|---|---|---|---|---|---|---|---|---|
| **'evaporation' to 'early roast'** | 44 | 219 | 170 | 198 | n.a. | | 150 | 180 |
| | 219 | 216 | 198 | 156 | | | 180 | 135 |
| | 216 | 203 | 156 | 184 | | | 135 | 136 |
| | 203 | 224 | | | | | 136 | 151 |
| | 224 | 77 | | | | | | |
| **'early roast' to 'late roast'** | 77 | 119 | 82 | 170 | 118 | 119 | 111 | 138 |
| | 119 | 106 | 170 | 59 | 119 | 67 | 138 | 124 |
| | 106 | 105 | 59 | 150 | 67 | 91 | 124 | 161 |
| | 105 | 133 | 150 | 156 | 91 | 167 | 161 | 131 |
| | 133 | 46 | 156 | 136 | 167 | 94 | 131 | 108 |
| **'late roast' to 'overroast'** | 77 | 91 | 89 | 174 | 108 | 94 | 181 | 180 |
| | 91 | 169 | 174 | 94 | 94 | 64 | 180 | 136 |
| | 169 | 105 | 94 | 108 | 64 | 68 | 136 | 205 |
| | 105 | 158 | 108 | 138 | 68 | 65 | 205 | 218 |
| | 158 | 181 | 138 | 160 | 65 | 78 | 218 | 197 |

**Table S2.** Molecular assignments of m/z of pairs for LDA. If no reference is indicated, the respective m/z is assigned based on references for Table 1.

| SPI at 118 nm | REMPI at 227 nm | REMPI at 248 nm | REMPI at 266 nm |
|---|---|---|---|
| 44 acetaldehyde | 59 $C_3$-amine | 64 | 108 methylvinylfuran, benzenediol[2] |
| 46 ethanol[3] | 82 $C_1$-furan | 65 | 111 trimethyloxazole[4] |
| 77 fragment of benzene derivatives | 89 | 67 pyrrole | 124 guaiacol, methyl-benzenediol[2] |
| 91 benzyl/tropylium cation | 94 phenol, dimethylsulfide[3], 4-methylpyrimidine[4] | 68 furan, pyrazole | 131 methylindole[4] |
| 105 fragment of benzaldehyde | 108 methylvinylfuran, $C_2$-pyrazine[3], benzenediol[2] | 78 benzene[4] | 135 aminoacetophenone[4], $C_4$-pyridine[4], benzothiazole[4] |
| 106 benzaldehyde | 136 4 vinyl-1,2-benzenediol[2], $C_4$-pyrazine[3], phenylacetic acid[4] | 91 benzyl/tropylium cation | 136 4 vinyl-1,2-benzenediol[2], $C_3$-pyridine[4], phenylacetic acid[4] |
| 119 indoline[4], benzoxazole[4] | 138 dihydroxybenzaldehyde[2], 4-methylguaiacol[4], 4-ethylcatechol[2] | 94 phenol, dimethylsulfide[3], 4-methylpyrimidine[4] | 138 dihydroxybenzaldehyde[2], 4-methylguaiacol[4], 4-ethylcatechol[2] |
| 133 methyl-indoline[4], methyl-benzoxazole[4] | 150 vinylguaiacol, $C_5$-pyrazine[4], phenylethylformiate[4] | 108 methylvinylfuran, $C_2$-pyranzine[3], benzenediol[2] | 150 vinylguaiacol, phenylethylformiate[4] |
| 158 nonanic acid[2], 2-heptyl acetate[4] | 156 2-ethylnaphthalene[4] | 118 benzofuran[4], indane[4] | 151 $^{13}$C-isotope of vinyl-guaiacol |
| 169 | 160 furfuryl-methyldisulfide[4], 2-furanyl-3-methylpyrazine[4] | 119 indoline[4], benzoxazole[4] | 161 $C_1$-furfurylpyrrole[4] |
| 181 | 170 $C_3$-naphthalene, 3,4,5-trihydroxybenzoic acid[4] | 167 | 180 caffeic acid[4], vinylsyringol[4], dimethoxy-acetophenone[4] |
| 203 | 174 5-(2-furyl)-2,3-dimethyl-pyrazine[4] | | 181 $^{13}$C-isotope of caffeic acid[4] |
| 216 | 184 $C_4$-naphthalene | | 197 |
| 219 | 198 $C_5$-naphthalene | | 205 5-acetyl-2,4-dimethyloxazole[4] |
| 224 sinapinic acid[4] | | | 218 |

## References


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