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Supplementary Material

Highly informative fingerprinting of extra-virgin olive oil volatiles: The role of high concentration-capacity sampling in combination with comprehensive two-dimensional gas chromatography

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The supplementary material comprises:

One Supplementary Figure and Two Supplementary Tables:

Supplementary Figure 1 SF1: schematic diagram of the combined untargeted/targeted *(UT) fingerprinting* workflow from Stilo, F., Liberto, E., Reichenbach, S. E., Tao, Q., Bicchi, C., & Cordero, C. (2019). Untargeted and targeted fingerprinting of extra virgin olive oil volatiles by comprehensive two-dimensional gas chromatography with mass spectrometry: Challenges in long-term studies. Journal of Agricultural and Food Chemistry, 67(18), 5289-5302. doi:10.1021/acs.jafc.9b01661.

Table ST1: Precision data on retention times and targeted 2D-peaks normalized volumes expressed as % Relative Standard Deviation (RSD).

Table ST2: 2D-peaks response descriptors comparison between 0.1 g and 1.5 g of olive oil HS-SPME-TRIF sampling amount.

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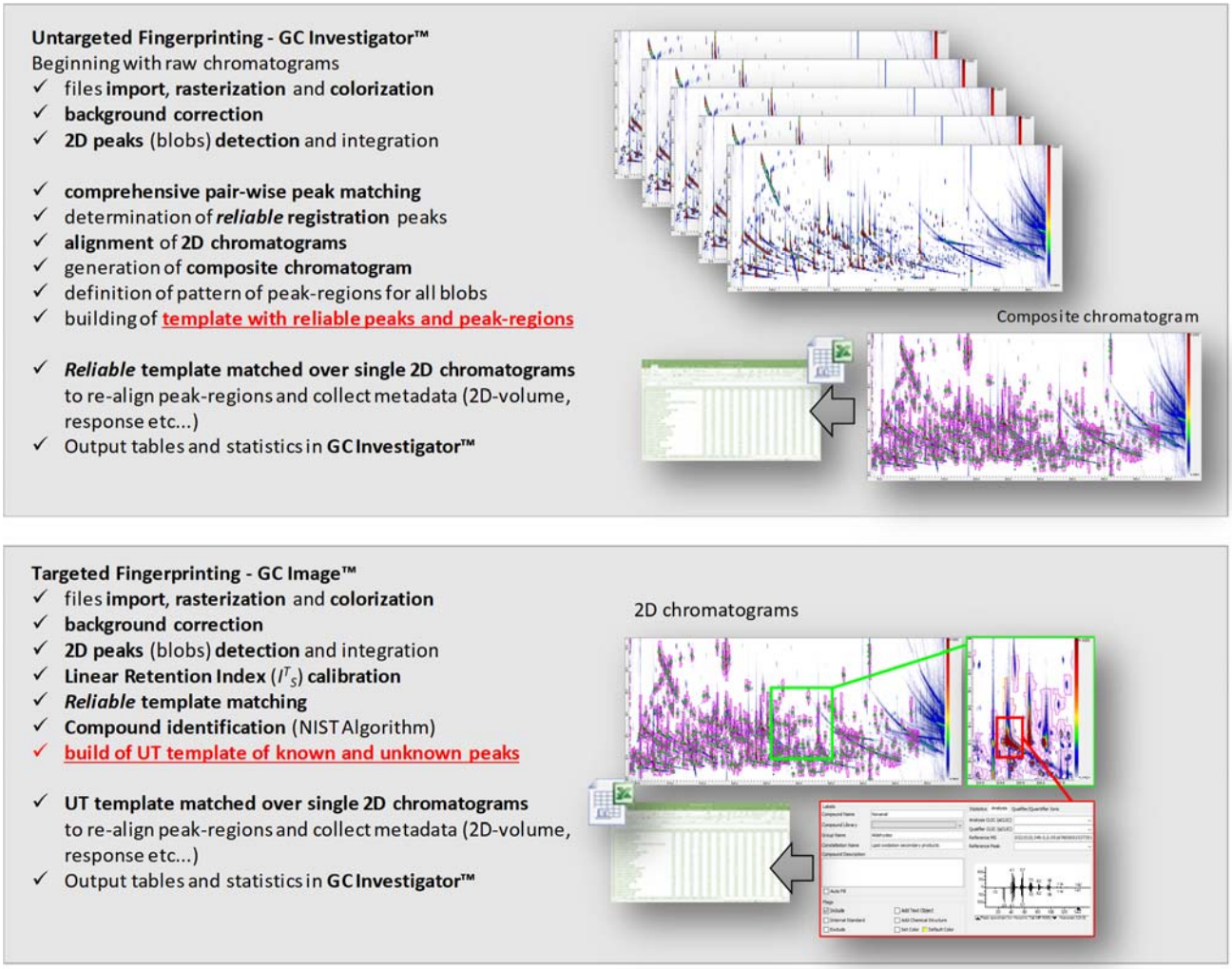

Supplementary table 1 ST1: Precision data on retention times and targeted 2D-peaks normalized volumes expressed as % Relative Standard Deviation (RSD). For those peaks that were not detected the "n.d." abbreviation is used.

	%RSD		%RSD on Normalized Volumes				
Compounds	$^{1}t_R$ (min)	$^{2}t_R$ (s)	**SPME-TRIF**	**DHS-PDMS**	**MMSE-ODS/GC**	**HSSE-PDMS/CPB**	**HSSE-TW2**
Hexanal	0.19	3.27	2.07	2.37	3.05	2.09	1.80
Heptanal	0.58	2.77	3.53	3.98	0.37	3.15	1.50
Octanal	0.36	3.97	3.27	4.38	1.37	4.40	2.02
Nonanal	0.10	1.53	2.66	2.82	1.46	3.94	4.30
Decanal	0.25	2.11	4.44	5.27	2.98	3.54	5.98
Undecanal	0.16	2.34	2.38	1.88	1.35	2.36	4.81
Dodecanal	0.27	3.20	3.30	1.53	3.03	4.43	0.65
Tridecanal	0.99	2.18	1.16	5.76	5.76	2.30	3.46
Tetradecanal	0.09	3.00	4.12	1.87	4.92	4.08	3.09
Pentadecanal	0.42	2.46	n.d.	3.30	n.d.	4.97	n.d.
Hexadecanal	0.21	1.18	n.d.	3.69	n.d.	n.d.	n.d.
Heptadecanal	0.03	2.06	n.d.	4.72	n.d.	n.d.	n.d.
Ethanol	0.93	3.69	0.29	0.23	0.63	4.32	2.93
2-Methyl-1-propanol	1.40	0.39	n.d.	1.07	1.89	n.d.	n.d.
1-Butanol	0.17	0.11	1.45	5.53	4.98	3.35	1.23
3-Methyl-1-butanol	0.22	3.43	2.97	4.51	4.29	3.89	5.83
1-Pentanol	1.06	3.62	3.19	5.37	3.87	2.30	3.10
(E)-1-Penten-3-ol	0.16	0.59	2.07	1.66	1.10	3.59	3.03
1-Hexanol	0.01	2.23	4.65	4.77	4.18	5.75	5.35
(Z)-3-Hexen-1-ol	0.01	3.45	0.23	3.51	3.41	3.65	4.31
(E)-3-Hexen-1-ol	0.35	2.79	0.80	5.79	3.38	2.08	3.88
1-Heptanol	0.23	2.40	1.85	3.83	1.97	3.11	3.69
1-Octanol	0.35	3.22	1.83	3.36	3.65	3.03	2.36
Phenethyl alcohol	0.22	3.82	3.66	4.11	5.93	5.44	2.08
1-Nonanol	0.01	3.83	2.84	1.01	1.30	6.06	2.49
1-Decanol	0.35	3.55	0.45	2.82	5.80	0.63	3.95
1-Undecanol	0.01	3.37	1.24	0.25	4.74	1.65	4.69
1-Dodecanol	0.28	2.08	2.37	4.62	3.74	0.93	3.01
1-Tridecanol	0.01	2.53	1.94	1.90	1.07	4.08	1.37
1-Tetradecanol	0.29	1.89	n.d.	4.91	0.73	3.21	4.52
Acetic acid	0.12	1.07	3.45	4.27	1.02	n.d.	1.82
Propanoic acid	0.32	3.57	4.21	3.96	0.86	n.d.	4.49
Butanoic acid	0.82	3.04	2.46	5.35	5.38	n.d.	1.79
Pentanoic acid	0.33	2.75	0.60	1.81	2.49	2.55	4.90
Hexanoic acid	0.62	2.69	2.24	1.80	5.51	0.96	5.80
Heptanoic acid	0.23	1.26	1.61	1.71	3.69	1.42	1.38
Octanoic acid	0.19	3.79	2.39	4.32	2.27	3.82	0.56
Nonanoic acid	0.13	3.63	2.35	4.44	3.39	2.36	5.12
Decanoic acid	0.57	3.13	1.92	1.38	5.00	4.86	1.86
Average	*0.33*	*2.42*	*2.35*	*3.33*	*3.07*	*3.30*	*3.23*

Supplementary table 2 ST2: 2D-peaks response descriptors comparison between 0.100 g and 1.500 g of olive oil HS-SPME-TRIF sampling amount.

Compound	^1t_R (min)	^2t_R (s)	I^T	0.1 g		1.5 g	
				Normalized Volume	Percent Response	Normalized Volume	Percent Response
Heptane	4.34	1.09	750	3.57	0.06	4.66	0.08
Octane	5.59	1.89	800	55.84	0.88	59.74	1.00
Ethyl acetate	6.75	1.35	850	0.90	0.01	0.13	0.00
Butanal	7.00	1.04	857	3.46	0.05	2.98	0.05
Ethanol	7.67	1.14	883	31.78	0.50	60.02	1.00
Pentanal	7.75	1.35	892	7.22	0.11	7.43	0.12
Nonane	7.82	2.34	895	3.25	0.05	3.06	0.05
3,4-Diethyl-1,5-hexadiene (RS+SR)	8.50	2.36	917	4.57	0.07	5.49	0.09
3,4-Diethyl-1,5-hexadiene (meso)	8.66	2.40	923	4.72	0.07	5.67	0.09
3-Pentanone	8.84	1.47	930	6.89	0.11	7.39	0.12
(*Z*)-3-Ethyl-1,5-octadiene	9.92	2.61	973	33.38	0.53	40.13	0.67
1-Penten-3-one	10.17	1.47	983	5.01	0.08	7.15	0.12
(*E*)-3-Ethyl-1,5-octadiene	10.42	2.61	993	32.12	0.51	37.66	0.63
Ethyl butanoate	10.59	1.77	1000	0.47	0.01	0.41	0.01
(*E*)-2-Butenal	10.75	1.38	1010	4.71	0.07	10.72	0.18
Butyl acetate	12.00	1.73	1046	0.51	0.01	0.45	0.01
Hexanal	12.25	1.77	1054	120.53	1.91	115.74	1.93
(*E,Z*)-3,7-Decadiene	12.25	2.74	1054	35.90	0.57	45.63	0.76
(*E,E*)-3,7-Decadiene	12.58	2.74	1065	29.27	0.46	31.56	0.53
(*E*)-Pent-2-enal	14.08	1.52	1110	12.93	0.20	19.81	0.33
Ethyl benzene	14.25	1.78	1115	0.41	0.01	0.40	0.01
1-Penten-3-ol	14.70	0.20	1129	18.30	0.29	21.22	0.35
1-Butanol	15.42	1.26	1142	1.38	0.02	1.19	0.02
Heptanal	16.50	1.89	1169	10.64	0.17	10.26	0.17
Limonene	16.91	2.15	1181	21.18	0.34	27.24	0.46
1-Pentanol	17.17	1.45	1190	4.32	0.07	6.11	0.10
(*Z*)-2-Hexenal	17.54	1.61	1198	28.72	0.45	38.53	0.64
(*E*)-2-Hexenal	18.00	1.64	1208	355.02	5.62	404.36	6.75
3-Methylbutan-1-ol	18.35	0.94	1215	6.56	0.10	7.90	0.13
1-Hexanol	19.00	1.71	1231	70.06	1.11	79.22	1.32
Styrene	19.25	1.35	1237	14.54	0.23	18.44	0.31
Hexyl acetate	20.33	2.02	1263	2.32	0.04	2.32	0.04
Octanal	21.08	2.02	1280	22.23	0.35	23.85	0.40
1-Octen-3-one	21.58	1.89	1292	18.05	0.29	21.03	0.35
(Z)-2-Penten-1-ol	21.75	1.22	1296	3.93	0.06	5.16	0.09
(*E*)-4,8-Dimethyl-1,3,7-nonatriene	21.92	2.36	1300	0.69	0.01	0.82	0.01
(*Z*)-3-Hexen-1-ol acetate	22.08	1.68	1304	97.50	1.54	110.07	1.84
(*E*)-2-Penten-1-ol	22.09	1.02	1304	23.65	0.37	27.27	0.46
1-Heptanol	22.31	1.89	1309	3.45	0.05	0.25	0.00
(*E*)-2-Heptenal	22.67	1.81	1317	35.14	0.56	41.96	0.70
6-Methylhept-5-en-2-one	23.17	1.85	1329	9.90	0.16	11.68	0.20
(*Z*)-3-Hexen-1-ol	24.08	1.30	1350	29.62	0.47	56.78	0.95
(*E*)-3-Hexen-1-ol	24.92	1.35	1369	1.70	0.03	5.49	0.09
1-Octanol	25.50	1.96	1383	7.99	0.13	9.36	0.16
α-Thujone	25.55	1.24	1384	100.00	1.58	100.00	1.67
Nonanal	25.75	2.19	1388	66.73	1.06	62.70	1.05
(*E,Z*)-2,4-Hexadienal	25.76	1.46	1388	15.20	0.24	16.97	0.28
(*E*)-2-Hexen-1-ol	25.92	1.26	1392	1.92	0.03	3.16	0.05
(*E,E*)-2,4-Hexadienal	26.00	1.48	1395	41.90	0.66	47.19	0.79
(*E*)-2-Octenal	27.25	1.89	1424	7.89	0.12	7.70	0.13
1-Octen-3-ol	27.83	1.47	1437	3.81	0.06	4.68	0.08
Acetic acid	28.50	0.97	1453	1.91	0.03	5.94	0.10
(*E,E*)-2,4-Heptadienal	28.75	1.73	1459	25.97	0.41	31.20	0.52
1-Nonanol	30.02	2.02	1487	2.87	0.05	3.63	0.06
Copaene	30.16	2.99	1492	27.60	0.44	31.42	0.52
Decanal	30.25	2.23	1494	21.71	0.34	18.96	0.32

(*E*)-Octa-3,5-dien-2-one	30.91	1.73	1507	6.16	0.10	7.28	0.12
(*E*)-2-Nonenal	31.75	1.98	1530	4.16	0.07	4.00	0.07
Propanoic acid	32.24	0.78	1541	4.98	0.08	2.31	0.04
Undecanal	34.49	2.02	1597	2.62	0.04	2.66	0.04
Methyl benzoate	34.91	1.43	1608	21.04	0.33	23.60	0.39
Butanoic acid	35.75	1.01	1630	2.61	0.04	1.63	0.03
(*E*)-2-Decenal	36.08	2.02	1638	21.61	0.34	23.97	0.40
1-Decanol	36.20	2.06	1642	1.49	0.02	1.89	0.03
γ-Hexalactone	37.91	1.56	1684	0.90	0.01	1.12	0.02
Dodecanal	38.65	2.12	1704	2.15	0.03	2.48	0.04
***α*-Farnesene**	40.15	2.23	1744	1.95	0.03	2.68	0.04
Pentanoic acid	40.16	1.05	1751	3.38	0.05	0.97	0.02
Phenylethyl alcohol	40.80	0.26	1763	9.45	0.15	11.18	0.19
1-Undecanol	41.93	2.10	1792	1.33	0.02	1.68	0.03
Tridecanal	42.57	2.24	1809	1.35	0.02	1.26	0.02
Hexanoic acid	44.16	1.01	1853	6.39	0.10	5.41	0.09
γ-Octalactone	45.66	1.77	1891	10.14	0.16	7.22	0.12
Tetradecanal	46.31	2.36	1914	1.21	0.02	1.09	0.02
1-Dodecanol	47.57	2.14	1951	0.19	0.00	0.24	0.00
Heptanoic acid	47.99	1.01	1963	3.93	0.06	1.95	0.03
Pentadecanal	49.89	2.48	2020	2.15	0.03	1.62	0.03
Octanoic acid	51.58	1.01	2072	3.59	0.06	0.32	0.01
1-Tridecanol	54.23	2.17	2155	0.34	0.01	0.43	0.01
Nonanoic acid	54.91	1.05	2176	7.35	0.12	5.56	0.09
Decanoic acid	58.24	1.05	2286	4.66	0.07	3.57	0.06
1-Tetradecanol	60.40	2.21	2361	1.37	0.02	1.34	0.02