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Comparison of an offline-SPE-GC-MS and online-HS-SPME-GC-MS method for the analysis of volatile terpenoids in wine

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Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1.

Figure S1a and S1b) The offline-SPE GC-MS chromatogram in spiked model wine (20 µg/L), spiked dearomatised white (20 µg/L) and a real white wine sample (ARV16S/B) respectively. **Figure S1b)** The online-HS-SPME GC-MS chromatogram in spiked model wine (20 µg/L), spiked dearomatised white (20 µg/L) and a real white wine sample (ARV16S/B) respectively.

Table S1. Precision and recovery (accuracy) results for the comparison of 3-octanol and 2,6-dimethyl-6-hepten-2-ol as internal standards.

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Table S5. Precision results by means of repeatability (%) for terpenoids quantitation at 100 µg/L for SPE and 2 µg/L for SPME for model (MW), white (WW) and red (RW) wine respectively.

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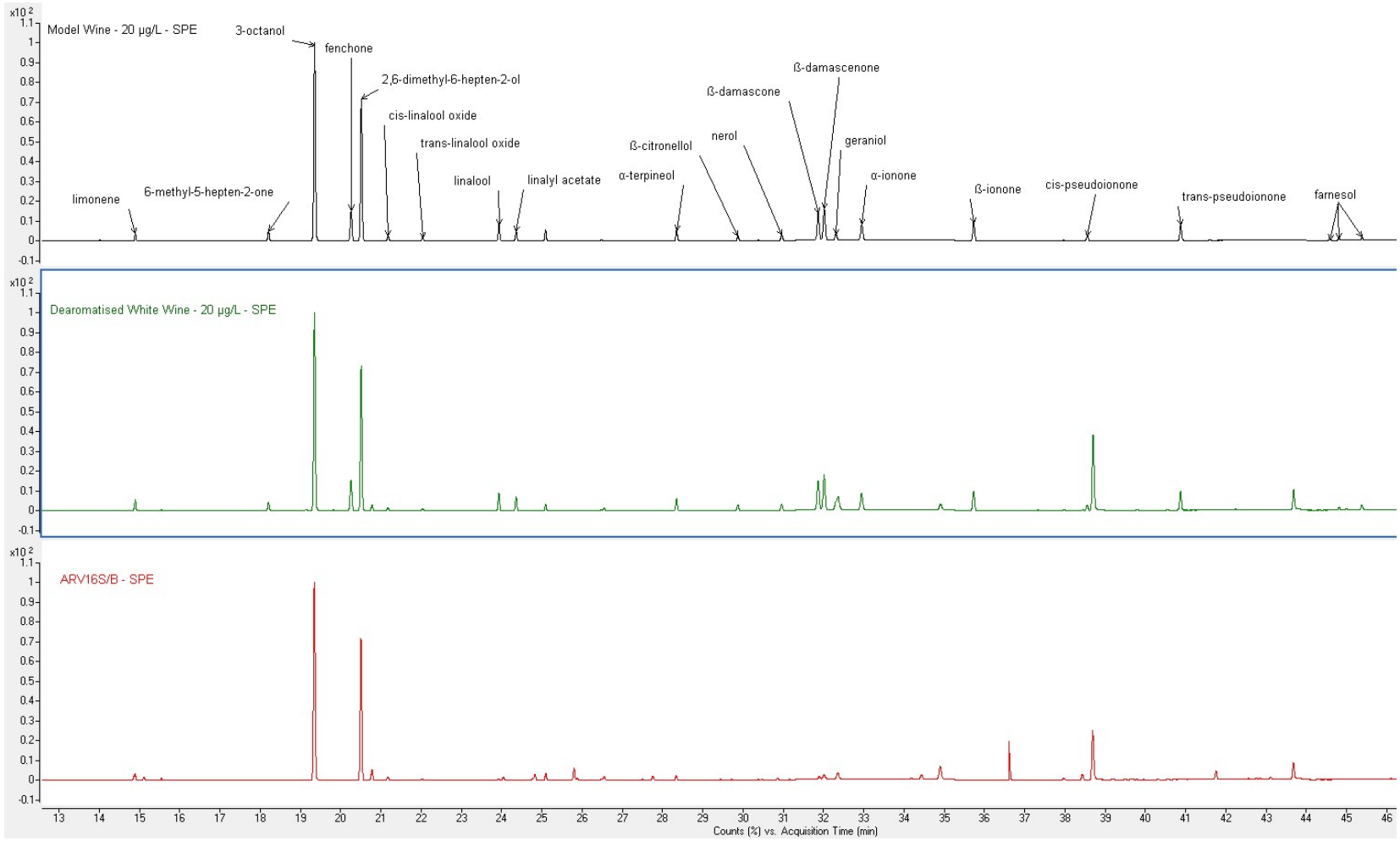

Figure S1a) The offline-SPE GC-MS chromatogram in spiked model wine (20 µg/L), spiked dearomatised white (20 µg/L) and a real white wine sample (ARV16S/B) respectively.

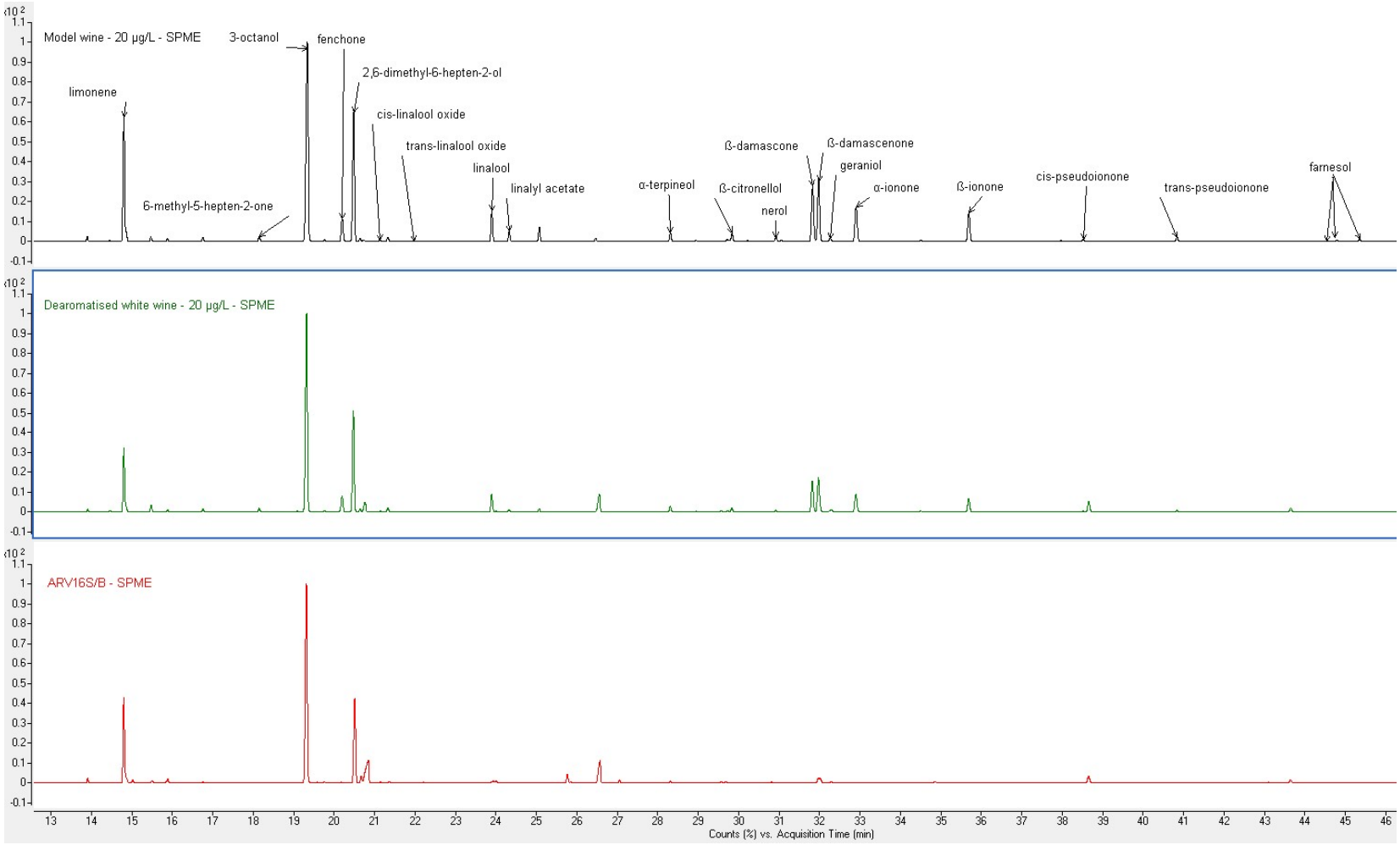

Figure S1b. The online-HS-SPME GC-MS chromatogram in spiked model wine (20 µg/L), spiked dearomatised white (20 µg/L) and a real white wine sample (ARV16S/B) respectively.

Table S1. Precision and recovery (accuracy) results for the comparison of 3-octanol and 2,6-dimethyl-6-hepten-2-ol as internal standards.

		SPE			SPME		
		MW	**WW**	**RW**	**MW**	**WW**	**RW**
3-Octanol (IS-1)	Precision[a] (%)	10.99	7.36	9.93	8.56	8.51	5.08
	Rt (%)	0.00591	0.00554	0.00635	0.00851	0.0106	0.00687
	R^2 (min)	0.9954	0.9934	0.9853	0.9798	0.9907	0.9434
	R^2 (max)	0.9997	0.9993	0.9998	0.9997	0.9998	0.9999
	Recovery - min (%)	83.20	81.03	89.81	88.96	87.32	82.37
	Recovery - max (%)	103.69	118.7	118.9	112.17	108.84	110.34
2,6-dimethyl-6-hepten-2-ol (IS-2)	Precision[a] (%)	12.63	7.96	11.83	12.89	9.908	6.054
	Retention time RSD (%)	0.00724	0.00469	0.00717	0.00685	0.0125	0.00737
	R^2 (min)	0.9912	0.9812	0.9839	0.9506	0.9814	0.9638
	R^2 (max)	0.9994	0.9997	0.9988	0.9983	0.9997	0.9996
	Recovery - min (%)	82.53	20.17	91.43	88.09	86.48	89.31
	Recovery - max (%)	101.91	134.67	136.5	149.89	148.25	149.31

[a] – Refers to the combined sample preparation and instrumental repeatability RSD (%)

[b] – Rt refers to the retention time RSD (%)

Table S2. Description and alcohol concentration of selected white wines used in this study.

Sample Code	Cultivar	Vintage	Alcohol (%)
FLY16S	Solaris	2016	14.5
ARV16S	Solaris	2016	14.0
ANI16/17S	Solaris	2016/2017	14.5
JCB16CH	Chardonnay	2016	12.5
FRN17SB	Sauvignon Blanc	2017	12.5
FLK17AL	Albariño	2017	13.0
KZC18CB	Chenin Blanc	2018	13.0
KLA16S	Solaris	2016	16.0
ORB17AL	Albariño	2017	12.5
LNC17SB	Sauvignon Blanc	2017	11.5
ARV16S/B	Solaris Barrique	2016	14.0
GWZ19C	Gewürztraminer	2019	11.0
GWC19E	Gewürztraminer	2019	11.0
MRF17SB	Sauvignon Blanc	2017	13.5

Table S3. Calculated (cRI) and literature retention indices (RI) for the analyses of terpenoids using both online HS-SPME and offline-SPE sample preparation methods.

Compound	RT (min)	cRI	RI	Ions (m/z)	
		(calc.)	(lit.)	Quant	Qual
(R)-(+)-Limonene	14.891	1220	1219	93	68
6-Methyl-5-hepten-2-one	18.207	1361	1359	108	111
Fenchone	20.260	1435	1422	152	81
cis-Linalool oxide (furanoid)	21.178	1466	1467	94	111
trans-Linalool oxide (furanoid)	22.036	1495	1490	94	111
Linalool	23.933	1562	1561	71	121
Linalyl acetate	24.364	1577	1575	121	93
α-terpineol	28.347	1724	1724	136	59
β-Citronellol	29.872	1783	1782	123	95
Nerol	30.966	1821	1806	123	95
β-Damascone	31.864	1851	1824	177	192
β-Damascenone	32.018	1856	1827	121	190
Geraniol	32.312	1866	1832	121	84
α-Ionone	32.948	1887	1844	121	192
β-Ionone	35.731	1879	1889	177	192
cis-PseudoIonone	38.556	-	-	69	124
trans-PseudoIonone	40.872	-	2073	69	124
Farnesol (*Z*,*E*)	44.578	-	2355	69	81
Farnesol (*E*,*Z*)	44.816	-	2329	69	81
Farnesol (*E*,*E*)	45.382	-	2355	69	81

Table S4. Accuracy results by means of recovery (%) for terpenoids quantitation at 100 μg/L for SPE and 2 μg/L for SPME for model (MW), white (WW) and red (RW) wine respectively.

Accuracy (recovery, n = 3)	SPE		SPME	
	100 μg/L		2 μg/L	
	WW	RW	WW	RW
Limonene	82	122	107	114
6-Methyl-5-hepten-2-one	102	109	133	145
Fenchone	95	94	124	141
cis-Linalool oxide	152	147	84	95
trans-Linalool oxide	161	155	98	94
Linalool	105	92	118	131
Linalyl acetate	75	81	142	123
α-Terpineol	110	99	108	124
β-Citronellol	106	94	105	152
Nerol	104	91	104	132
β-Damascone	95	90	102	128
β-Damascenone	93	90	92	106
Geraniol	96	86	101	146
α-Ionone	95	92	106	141
β-Ionone	94	89	116	116
cis-Pseudoionone	104	93	159	145
trans-Pseudoionone	98	91	120	111
Farnesol (*Z*,*E*)	83	77	139	128
Farnesol (*E*,*Z*)	85	78	108	130
Farnesol (*E*,*E*)	80	73	120	107

Table S5. Precision results by means of repeatability (%) for terpenoids quantitation at 100 μg/L for SPE and 2 μg/L for SPME for model (MW), white (WW) and red (RW) wine respectively.

Precision (repeatability, n = 3)	SPE			SPME		
	100 μg/L			2 μg/L		
	MW	WW	RW	MW	WW	RW
Limonene	11.9	8.3	6.8	5.9	5.7	5.1
6-Methyl-5-hepten-2-one	3.9	6.6	5.9	0.9	3.3	2.3
Fenchone	3.9	6.0	5.7	1.6	3.8	8.7
cis-Linalool oxide	2.9	6.6	3.6	2.8	1.6	4.1
trans-Linalool oxide	2.9	6.5	3.9	3.0	1.6	4.4
Linalool	3.5	4.9	4.9	2.4	4.1	3.9
Linalyl acetate	3.4	6.2	6.5	9.6	13.3	9.8
α-Terpineol	2.9	4.6	5.3	6.4	0.8	3.6
β-Citronellol	3.2	4.7	4.8	4.9	4.6	6.4
Nerol	3.0	4.6	6.3	5.5	5.6	8.5
β-Damascone	3.6	5.4	6.7	4.1	1.2	7.4
β-Damascenone	3.8	5.6	6.7	3.5	1.1	8.1
Geraniol	2.7	5.5	6.2	4.4	8.9	16.1
α-Ionone	3.8	5.4	6.7	5.1	1.2	8.1
β-Ionone	3.5	5.3	6.9	6.7	1.5	8.2
cis-Pseudoionone	3.7	5.4	7.9	9.0	7.0	6.0
trans-Pseudoionone	3.3	5.7	8.0	10.0	14.6	12.7
Farnesol (*Z*,*E*)	4.5	5.5	8.3	18.2	7.2	27.6
Farnesol (*E*,*Z*)	3.0	6.0	8.4	17.0	16.7	15.6
Farnesol (*E*,*E*)	3.0	6.5	10.7	18.0	15.8	14.1