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Assay data

Ethanol

Table S1. Mean Δ absorbance values for ethanol standards and ice fraction samples.

	Ethanol standard concentration (% *v/v*)					Sample		
	0	**2**	**3**	**4**	**5**	**S1$_{ice}$**	**S2$_{ice}$**	**S3$_{ice}$**
Mean Δ absorbance	0.000	0.904	1.210	1.490	1.690	1.89	1.93	1.90
Ethanol concentration (% *v/v*)	-	-	-	-	-	5.1*	5.3*	5.2*

* Sample ethanol concentration calculated from Figure S1 ice fraction sample calibration curve.

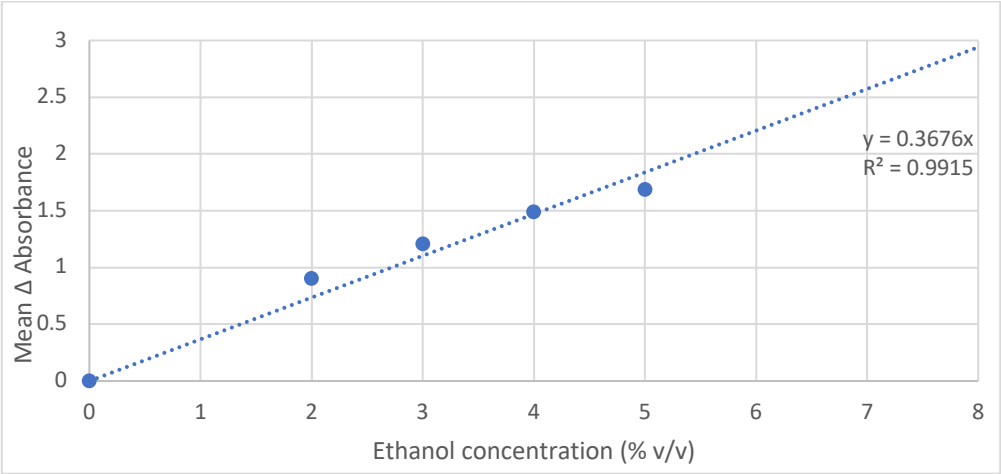


Figure S1. Ice fraction sample calibration curve.

Regression line: $y = 0.3676x$

Ice fraction sample ethanol concentration: $x = y/0.3676$

Mean ice fraction ethanol concentration: (5.1 + 5.3 + 5.2)/3 = 5.2 % *v/v*

Table S2. Mean Δ absorbance values for ethanol standards and control samples.

	Ethanol standard concentration (% *v/v*)						Sample		
	0	**10**	**12**	**14**	**16**	**NC**	**PC1**	**PC2**	**PC3**
Mean Δ absorbance	0.000	0.371	0.462	0.552	0.623	0.425	0.430	0.432	0.426
Ethanol concentration (% *v/v*)	-	-	-	-	-	11.0*	11.1*	11.2*	11.0*

* Sample ethanol concentration calculated from Figure S2 control sample calibration curve.

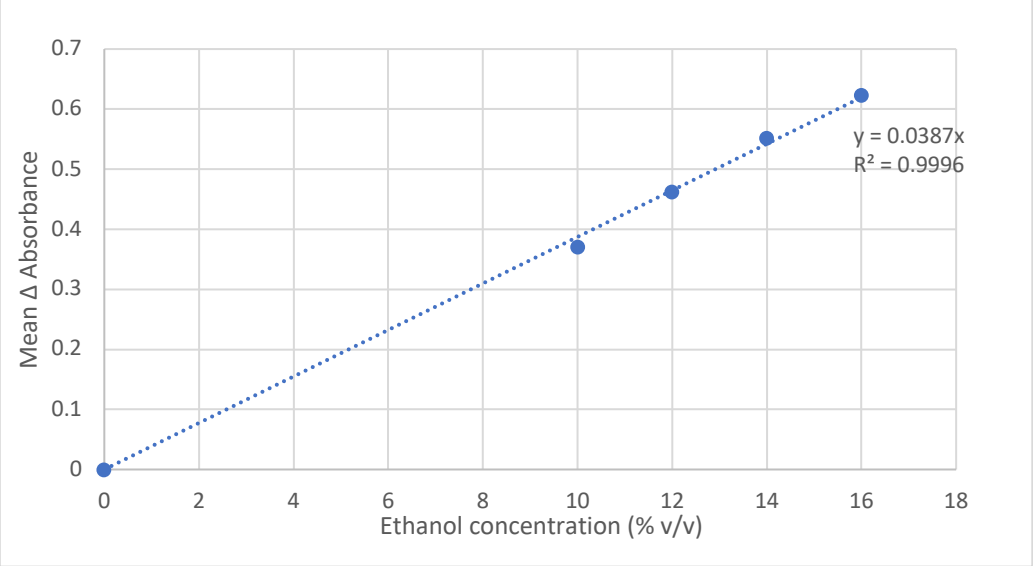


Figure S2. Control sample calibration curve.

Regression line: $y = 0.0387x$

Control sample ethanol concentration: $x = y/0.0387$

Mean control ethanol concentration: (11.1 + 11.2 + 11.0)/3 = 11.1 % *v/v*

pH and TA

Table S3. pH and TA results.

Sample	pH	Temperature (°C)	Sodium hydroxide titre (mL)				TA (g/L as tartaric acid)
			1	2	3	Mean	
NC	3.70	20.5	6.67	6.51	6.44	6.54	4.91
PC1	3.69	18.6	6.53	6.73	6.64	6.63	4.98
PC2	3.71	17.9	6.51	6.32	6.28	6.37	4.78
PC3	3.72	18.0	6.23	6.13	6.14	6.17	4.63
$S1_{ice}$	3.68	19.4	5.31	5.23	5.23	5.26	3.95
$S2_{ice}$	3.66	19.2	5.08	5.09	5.08	5.08	3.81
$S3_{ice}$	3.67	19.0	5.11	5.13	5.13	5.12	3.84

Modified Somers colour assay

Table S4. Modified Somers buffer treatment absorbance results.

	1		2		3		Average		Average * Dilution factor	
Sample	A420 (au)	A520 (au)	A420 (au)	A520 (au)	A420 (au)	A520 (au)	A420 (au)	A520 (au)	A420 (au)	A520 (au)
NC	0.350	0.439	0.350	0.429	0.353	0.439	0.351	0.436	3.861	4.792
PC1	0.390	0.472	0.380	0.460	0.377	0.455	0.382	0.462	4.206	5.086
PC2	0.393	0.472	0.387	0.469	0.385	0.464	0.388	0.468	4.272	5.152
PC3	0.398	0.480	0.398	0.477	0.386	0.464	0.394	0.474	4.334	5.210
$S1_{ice}$	0.323	0.388	0.321	0.388	0.319	0.384	0.321	0.387	3.531	4.253
$S2_{ice}$	0.311	0.376	0.314	0.381	0.315	0.378	0.313	0.378	3.447	4.162
$S3_{ice}$	0.323	0.387	0.324	0.390	0.319	0.384	0.322	0.387	3.542	4.257

Dilution factor = 11

Table S5. Modified Somers sulfite treatment absorbance results.

	1	2	3	Average	Average * Dilution factor
Sample	**A520 (au)**	**A520 (au)**	**A520 (au)**	**A520 (au)**	**A520 (au)**
NC	0.417	0.394	0.392	0.401	4.415
PC1	0.419	0.397	0.398	0.405	4.455
PC2	0.429	0.414	0.401	0.415	4.565
PC3	0.436	0.408	0.401	0.415	4.569
$S1_{ice}$	0.373	0.337	0.342	0.351	3.861
$S2_{ice}$	0.348	0.351	0.324	0.341	3.754
$S3_{ice}$	0.337	0.357	0.333	0.342	3.769

Dilution factor = 11.01

Table S6. Modified Somers ethanal treatment absorbance results.

	1		2		3		Average		Average * Dilution factor	
Sample	**A420 (au)**	**A520 (au)**	**A420 (au)**	**A520 (au)**	**A420 (au)**	**A520 (au)**	**A420 (au)**	**A520 (au)**	**A420 (au)**	**A520 (au)**
NC	0.332	0.453	0.332	0.451	0.336	0.453	0.333	0.452	3.670	4.980
PC1	0.366	0.464	0.350	0.452	0.339	0.452	0.352	0.456	3.872	5.021
PC2	0.365	0.447	0.354	0.450	0.353	0.448	0.357	0.448	3.934	4.936
PC3	0.357	0.452	0.340	0.445	0.357	0.456	0.351	0.451	3.868	4.966
$S1_{ice}$	0.302	0.388	0.296	0.383	0.301	0.384	0.300	0.385	3.299	4.239
$S2_{ice}$	0.294	0.375	0.282	0.364	0.284	0.363	0.287	0.367	3.156	4.044
$S3_{ice}$	0.288	0.372	0.292	0.376	0.291	0.371	0.290	0.373	3.197	4.107

Dilution factor = 11.01

Table S7. Modified Somers hydrochloric acid treatment absorbance results.

	1		2		3		Average		Average * Dilution factor	
Sample	**A280 (au)**	**A520 (au)**	**A280 (au)**	**A520 (au)**	**A280 (au)**	**A520 (au)**	**A280 (au)**	**A520 (au)**	**A280 (au)**	**A520 (au)**
NC	0.993	0.242	0.963	0.240	0.951	0.244	0.969	0.242	49.419	12.342
PC1	0.958	0.235	0.987	0.245	1.021	0.253	0.989	0.244	50.422	12.461
PC2	0.959	0.237	1.014	0.245	1.023	0.248	0.999	0.243	50.932	12.410
PC3	0.967	0.233	0.983	0.240	1.000	0.245	0.983	0.239	50.150	12.206
$S1_{ice}$	0.865	0.209	0.830	0.199	0.823	0.202	0.839	0.203	42.806	10.370
$S2_{ice}$	0.804	0.198	0.812	0.202	1.022	0.232	0.879	0.211	44.846	10.744
$S3_{ice}$	0.832	0.207	0.836	0.209	0.817	0.203	0.828	0.206	42.245	10.523

Dilution factor = 51

Table S8. Summary of mean absorbance results for modified Somers colour assay.

	Buffer		Sulfite	Ethanal		Hydrochloric acid	
Sample	**A420 (au)**	**A520 (au)**	**A520 (au)**	**A420 (au)**	**A520 (au)**	**A280 (au)**	**A520 (au)**
NC	0.350	0.439	0.429	0.353	0.439	0.351	0.436
PC1	0.390	0.472	0.460	0.377	0.455	0.382	0.462
PC2	0.393	0.472	0.469	0.385	0.464	0.388	0.468
PC3	0.398	0.480	0.477	0.386	0.464	0.394	0.474
$S1_{ice}$	0.323	0.388	0.388	0.319	0.384	0.321	0.387
$S2_{ice}$	0.311	0.376	0.381	0.315	0.378	0.313	0.378
$S3_{ice}$	0.323	0.387	0.390	0.319	0.384	0.322	0.387

Modified Somers colour assay calculations used for Table S9:

Chemical age 1 (no units): $\frac{A520\ sulphite}{A520\ ethanal}$

Chemical age 2 (no units): $\frac{A520\ sulphite}{A520\ HCl}$

Degree of ionisation of anthocyanin (%): $\frac{(A520\ buffer - A520\ sulphite)}{(A520\ HCl - 1) - (1.6667 \times A520\ sulphite)} \times 100$

Total anthocyanin (mg/L): $20 \times [A520\ HCl - (1.667 \times A520\ sulphite)]$

Colour density (au): $A420\ buffer + A520\ buffer$

Colour density, SO_2 corrected (au): $A420\ ethanal + A520\ ethanal$

Hue (no units): $\frac{A420\ buffer}{A520\ buffer}$

Total phenolics (au): $A280\ HCl - 4$

SO_2 resistant pigments (au): $A520\ sulphite$

Table S9. Modified Somers colour assay results.

Sample	Chemical age 1	Chemical age 2	Degree of ionisation of anthocyanin (%)	Total anthocyanin (mg/L)	Colour density (au)	Colour density, SO_2 corrected (au)	Hue	Total phenolics (au)	SO_2 resistant pigment (au)
NC	0.89	0.36	7.57	99.67	8.65	8.65	0.81	45.42	4.42
PC1	0.89	0.36	12.52	100.70	9.29	8.89	0.83	46.42	4.46
PC2	0.92	0.37	12.21	96.01	9.42	8.87	0.83	46.93	4.57
PC3	0.92	0.37	13.97	91.81	9.54	8.83	0.83	46.15	4.57
$S1_{ice}$	0.91	0.37	9.97	78.70	7.78	7.54	0.83	38.81	3.86
$S2_{ice}$	0.93	0.35	9.08	89.73	7.61	7.20	0.83	40.85	3.75
$S3_{ice}$	0.92	0.36	11.50	84.82	7.80	7.30	0.83	38.25	3.77

Folin–Ciocalteu

Table S10. Gallic acid standard solution absorbance results.

Gallic acid (mL)	De-ionised water (mL)	Gallic acid concentration (mg/L)	Absorbance at 765 nm (au)		
			1	2	Average
0	100	0	0.000	0.000	0.000
1	99	50	0.023	0.025	0.024
2	98	100	0.073	0.089	0.081
3	97	150	0.126	0.123	0.125
5	95	250	0.241	0.241	0.241
10	90	500	0.506	0.510	0.508
20	80	1,000	1.019	1.023	1.021

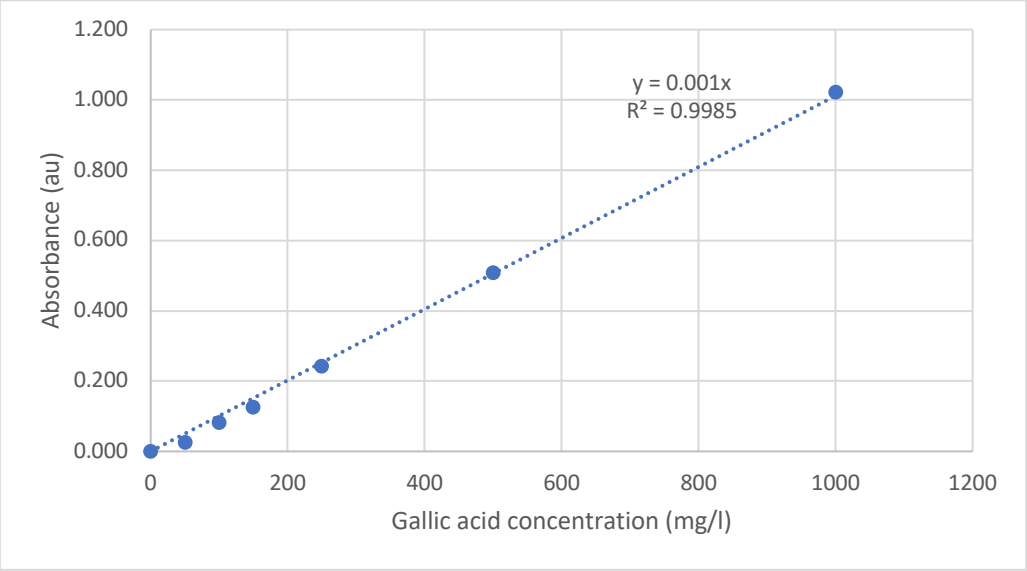


Figure S3. Gallic acid standard solution calibration curve.

Regression line: $y = 0.001x$

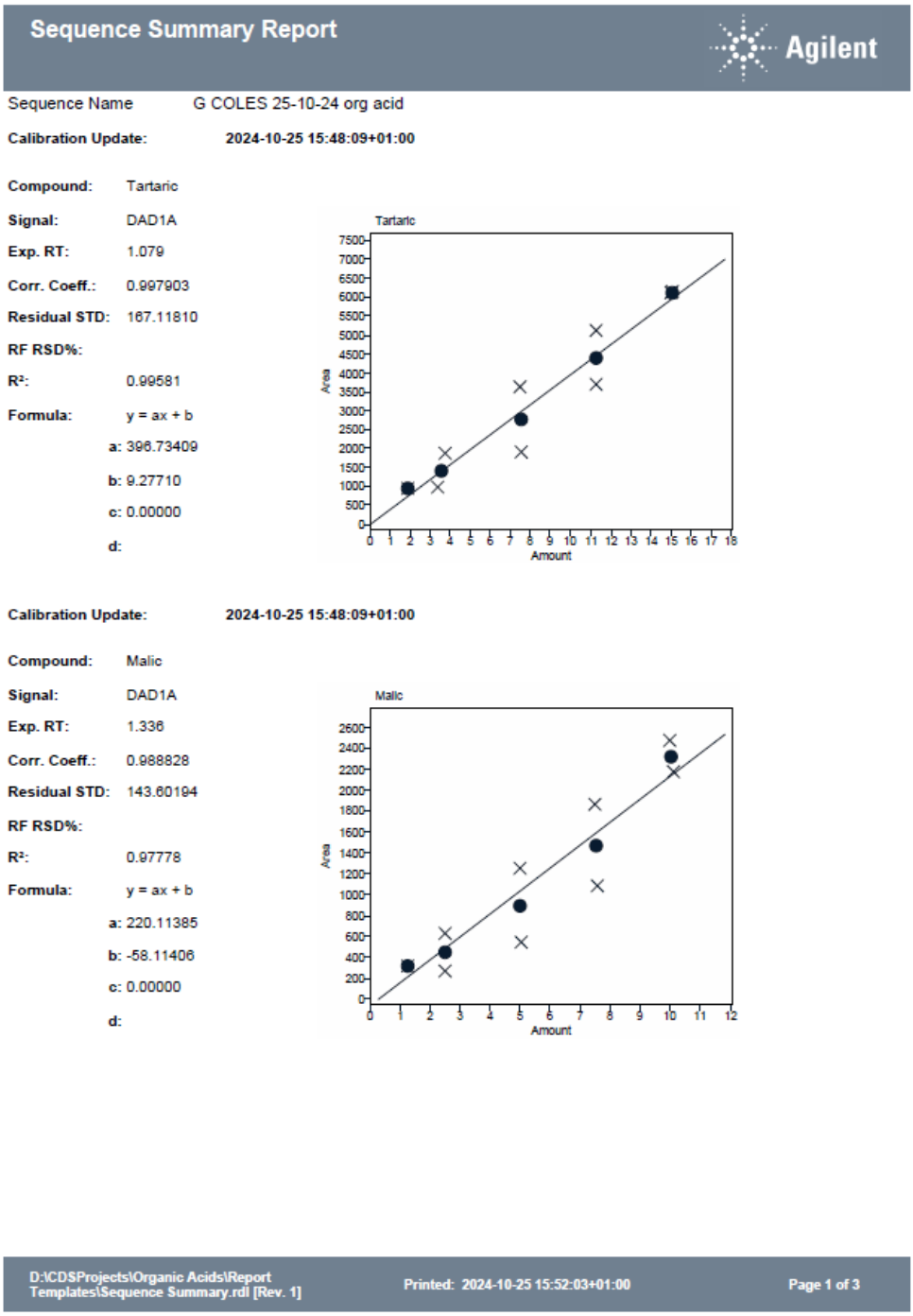
Table S11. Folin–Ciocalteu results.

Sample	1 A765 (au)	2 A765 (au)	3 A765 (au)	Average A765 (au)	Average * Dilution factor (au)	Concentration (mg/L GAE)
NC	0.226	0.239	0.235	0.233	2.33	2,333
PC1	0.234	0.238	0.243	0.238	2.38	2,383
PC2	0.234	0.244	0.237	0.238	2.38	2,383
PC3	0.236	0.238	0.243	0.239	2.39	2,390
$S1_{ice}$	0.193	0.206	0.205	0.201	2.01	2,013
$S2_{ice}$	0.190	0.185	0.191	0.189	1.89	1,887
$S3_{ice}$	0.190	0.203	0.186	0.193	1.93	1,930

GAE – Gallic acid equivalent

Dilution factor = 10

HPLC



Sequence Summary Report

Agilent

Sequence Name G COLES 25-10-24 org acid

Calibration Update: **2024-10-25 15:48:09+01:00**

Compound: Tartaric
Signal: DAD1A
Exp. RT: 1.079
Corr. Coeff.: 0.997903
Residual STD: 167.11810
RF RSD%:
R²: 0.99581
Formula: y = ax + b
a: 396.73409
b: 9.27710
c: 0.00000
d:

Calibration Update: **2024-10-25 15:48:09+01:00**

Compound: Malic
Signal: DAD1A
Exp. RT: 1.336
Corr. Coeff.: 0.988828
Residual STD: 143.60194
RF RSD%:
R²: 0.97778
Formula: y = ax + b
a: 220.11385
b: -58.11406
c: 0.00000
d:

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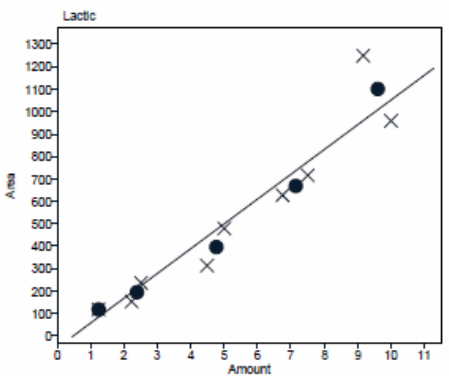
Figure S4. Summary report of HPLC results – page 1 of 3.

Sequence Summary Report

Agilent

Calibration Update: 2024-10-25 15:48:09+01:00

Compound: Lactic
Signal: DAD1A
Exp. RT: 1.628
Corr. Coeff.: 0.986320
Residual STD: 75.69900
RF RSD%:
R²: 0.97283
Formula: y = ax + b
a: 110.16563
b: -46.76446
c: 0.00000
d:



Name: Lactic

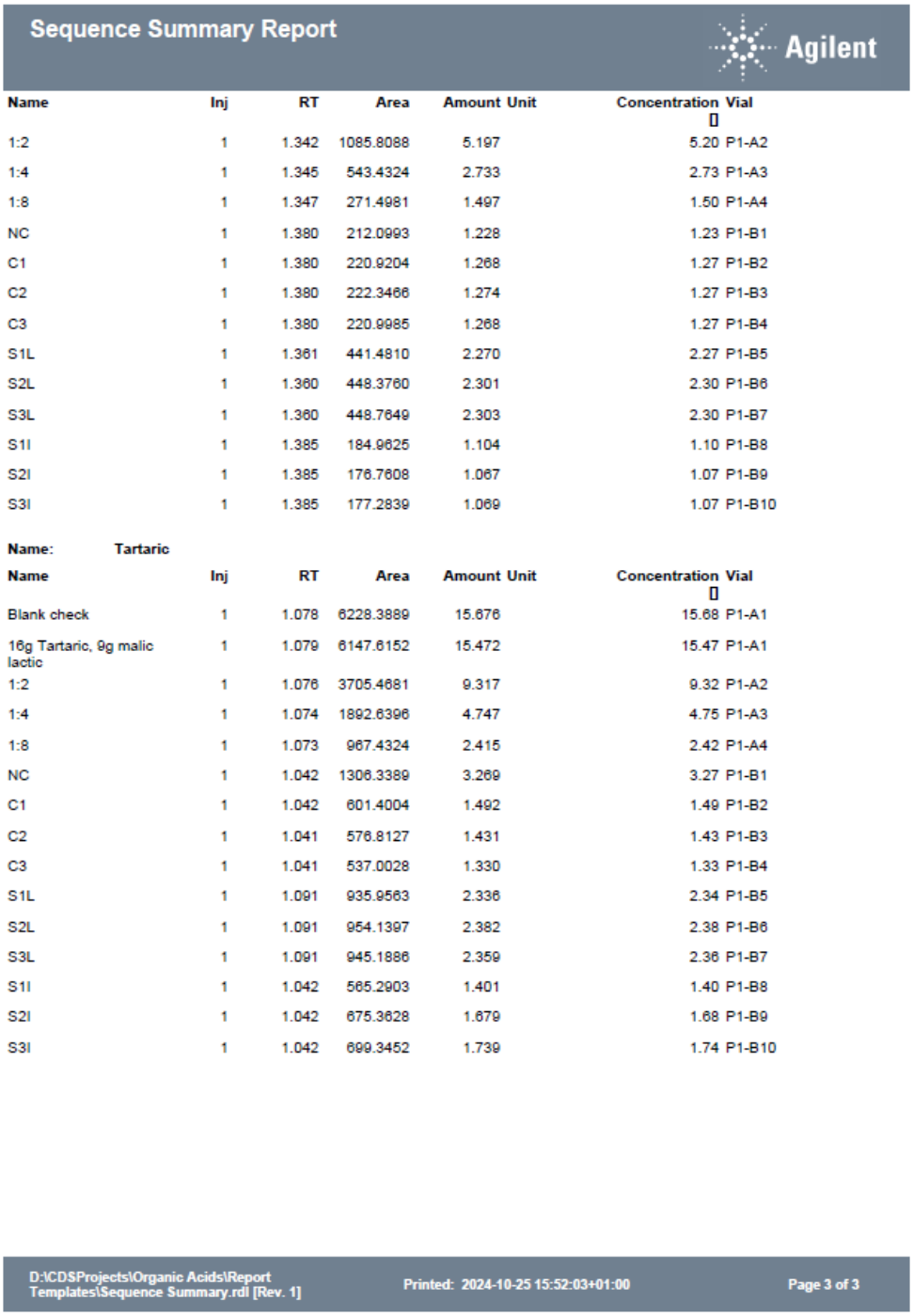
Name	Inj	RT	Area	Amount	Unit	Concentration []	Vial
Blank check	1	1.628	1252.3927	11.793		11.79	P1-A1
16g Tartaric, 9g malic lactic	1	1.628	1247.9694	11.753		11.75	P1-A1
1:2	1	1.637	625.0031	6.098		6.10	P1-A2
1:4	1	1.642	311.7881	3.255		3.25	P1-A3
1:8	1	1.644	155.6998	1.838		1.84	P1-A4
NC	1	1.681	94.4320	1.282		1.28	P1-B1
C1	1	1.677	109.6262	1.420		1.42	P1-B2
C2	1	1.675	111.6749	1.438		1.44	P1-B3
C3	1	1.679	102.7474	1.357		1.36	P1-B4
S1L	1						P1-B5
S2L	1						P1-B6
S3L	1						P1-B7
S1I	1	1.547	868.3180	8.306		8.31	P1-B8
S2I	1	1.548	856.9891	8.204		8.20	P1-B9
S3I	1	1.548	857.1937	8.205		8.21	P1-B10

Name: Malic

Name	Inj	RT	Area	Amount	Unit	Concentration []	Vial
Blank check	1	1.336	2180.4941	10.170		10.17	P1-A1
16g Tartaric, 9g malic lactic	1	1.336	2173.9858	10.141		10.14	P1-A1

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Figure S5. Summary report of HPLC results – page 2 of 3.



Sequence Summary Report

Agilent

Name	Inj	RT	Area	Amount	Unit	Concentration []	Vial
1:2	1	1.342	1085.8088	5.197		5.20	P1-A2
1:4	1	1.345	543.4324	2.733		2.73	P1-A3
1:8	1	1.347	271.4981	1.497		1.50	P1-A4
NC	1	1.380	212.0993	1.228		1.23	P1-B1
C1	1	1.380	220.9204	1.268		1.27	P1-B2
C2	1	1.380	222.3466	1.274		1.27	P1-B3
C3	1	1.380	220.9985	1.268		1.27	P1-B4
S1L	1	1.361	441.4810	2.270		2.27	P1-B5
S2L	1	1.360	448.3760	2.301		2.30	P1-B6
S3L	1	1.360	448.7649	2.303		2.30	P1-B7
S1I	1	1.385	184.9625	1.104		1.10	P1-B8
S2I	1	1.385	176.7608	1.067		1.07	P1-B9
S3I	1	1.385	177.2839	1.069		1.07	P1-B10

Name: **Tartaric**

Name	Inj	RT	Area	Amount	Unit	Concentration []	Vial
Blank check	1	1.078	6228.3889	15.676		15.68	P1-A1
16g Tartaric, 9g malic lactic	1	1.079	6147.6152	15.472		15.47	P1-A1
1:2	1	1.076	3705.4681	9.317		9.32	P1-A2
1:4	1	1.074	1892.6396	4.747		4.75	P1-A3
1:8	1	1.073	967.4324	2.415		2.42	P1-A4
NC	1	1.042	1306.3389	3.269		3.27	P1-B1
C1	1	1.042	601.4004	1.492		1.49	P1-B2
C2	1	1.041	576.8127	1.431		1.43	P1-B3
C3	1	1.041	537.0028	1.330		1.33	P1-B4
S1L	1	1.091	935.9563	2.336		2.34	P1-B5
S2L	1	1.091	954.1397	2.382		2.38	P1-B6
S3L	1	1.091	945.1886	2.359		2.36	P1-B7
S1I	1	1.042	565.2903	1.401		1.40	P1-B8
S2I	1	1.042	675.3628	1.679		1.68	P1-B9
S3I	1	1.042	699.3452	1.739		1.74	P1-B10

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Figure S6. Summary report of HPLC results – page 3 of 3.

In previous laboratory assays, an anomalous result associated with internal system pressure for the first reading had been observed, after which the pressure returned to normal levels. Consequently, a ‘Blank Check’ was included in the assay to mitigate false readings.

Summary

Table S12. Summary of sample observed mean results.

Sample	Ethanol (% v/v)	pH	Titratable acidity (g/L as tartaric acid)	Total phenol concentration (mg/L GAE)	Total phenolics (au)	Total anthocyanins (mg/L)	Colour density, SO_2 corrected (au)	Lactic acid concentration (g/L)	Malic acid concentration (g/L)	Tartaric acid concentration (g/L)
NC	11.0	3.70	4.91	2,333	45.42	99.67	8.65	1.28	1.23	3.27
PC1	11.1	3.69	4.98	2,383	46.42	100.70	8.89	1.42	1.27	1.49
PC2	11.2	3.71	4.78	2,383	46.93	96.01	8.87	1.44	1.27	1.43
PC3	11.0	3.72	4.63	2,390	46.15	91.81	8.83	1.36	1.27	1.33
$S1_{ice}$	5.1	3.68	3.95	2,013	38.81	78.70	7.54	8.31	1.10	1.40
$S2_{ice}$	5.3	3.66	3.81	1,887	40.85	89.73	7.20	8.20	1.07	1.68
$S3_{ice}$	5.2	3.67	3.84	1,930	38.25	84.82	7.30	8.21	1.07	1.74

GAE – Gallic acid equivalent

Table S13. Summary of treatment observed means.

Sample	Ethanol (% v/v)	pH	Titratable acidity (g/L as tartaric acid)	Total phenol concentration (mg/L GAE)	Total phenolics (au)	Total anthocyanins (mg/L)	Colour density, SO_2 corrected (au)	Lactic acid concentration (g/L)	Malic acid concentration (g/L)	Tartaric acid concentration (g/L)
Negative control	11.0	3.70	4.91	2,333	45.42	99.67	8.65	1.28	1.23	3.27
Positive control	11.1	3.71	4.79	2,386	46.50	96.18	8.87	1.41	1.27	1.42
Ice fraction	5.2	3.67	3.87	1,943	39.30	84.42	7.35	8.24	1.08	1.61

GAE – Gallic acid equivalent

Principal Component Analysis

Table S14. PCA eigenvalues.

	F1	F2	F3	F4	F5	F6
Eigenvalues	8.328	1.154	0.422	0.081	0.014	0.001
Variability %	83.284	11.540	4.219	0.812	0.137	0.008
Cumulative %	83.284	94.824	99.043	99.855	99.992	100.000

Table S15. PCA eigenvectors.

	F1	F2	F3	F4	F5
pH	0.300	–0.260	–0.616	–0.418	–0.213
TA (g/L)	0.339	0.103	0.068	0.580	0.194
Total phenol concentration (mg/L GAE)	0.346	0.008	0.012	–0.081	–0.228
Total phenolics (au)	0.342	–0.103	–0.120	0.287	0.026
Total anthocyanins (mg/L)	0.338	–0.034	0.230	–0.494	0.751
Colour density, SO_2 corrected (au)	0.291	0.342	0.597	–0.249	–0.428
Lactic acid concentration (g/L)	0.343	–0.100	–0.048	0.265	0.005
Malic acid concentration (g/L)	–0.346	–0.026	0.019	0.094	0.298
Tartaric acid concentration (g/L)	0.342	–0.139	–0.002	0.121	0.091

GAE – Gallic acid equivalent

Table S16. Contribution of variables (%).

	F1	F2	F3	F4	F5
pH	8.970	6.768	37.885	17.493	4.541
TA (g/L)	11.500	1.065	0.463	33.614	3.763
Total phenol concentration (mg/L GAE)	11.991	0.007	0.014	0.656	5.214
Total phenolics (au)	11.706	1.067	1.434	8.208	0.070
Total anthocyanins (mg/L)	11.392	0.117	5.304	24.390	56.397
Colour density, SO_2 corrected (au)	8.488	11.704	35.650	6.217	18.319
Lactic acid concentration (g/L)	11.789	1.001	0.227	7.002	0.003
Malic acid concentration (g/L)	11.969	0.069	0.035	0.877	8.908
Tartaric acid concentration (g/L)	11.724	1.919	0.001	1.466	0.823

GAE – Gallic acid equivalent

Table S17. Summary of squared cosines of the variables.

	F1	F2	F3	F4	F5
pH	0.747	0.078	0.160	0.014	0.001
TA (g/L)	0.958	0.012	0.002	0.027	0.001
Total phenol concentration (mg/L GAE)	0.999	0.000	0.000	0.001	0.001
Total phenolics (au)	0.975	0.012	0.006	0.007	0.000
Total anthocyanins (mg/L)	0.949	0.001	0.022	0.020	0.008
Colour density, SO_2 corrected (au)	0.707	0.135	0.150	0.005	0.003
Lactic acid concentration (g/L)	0.982	0.012	0.001	0.006	0.000
Malic acid concentration (g/L)	0.997	0.001	0.000	0.001	0.001
Tartaric acid concentration (g/L)	0.976	0.022	0.000	0.001	0.000

GAE – Gallic acid equivalent