Direct and interference-free determination of thirteen phenolic compounds in red wines using chemometrics-assisted HPLC-DAD strategy for the authentication of vintage year

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SUPPLEMENTARY DATA

Table A.1

The designed concentrations levels (μg mL^{-1}) of thirteen phenolic compounds in ten calibration samples (C01-10) and five prediction samples (P01-05)

Samples NO.	GA	CA	CFA	p-HBA	VA	FA	RES	MY	MO	QU	LU	KA	AP
C01	2.09	13.02	11.02	4.42	6.57	0.35	0.31	6.44	4.22	4.58	6.77	8.00	0.43
C02	6.26	11.65	9.86	9.55	2.53	6.65	1.34	5.76	9.72	9.67	2.61	7.16	1.88
C03	10.44	10.28	8.70	3.39	9.60	1.05	2.36	5.09	15.21	3.54	9.90	6.32	3.33
C04	14.62	8.94	7.54	8.53	5.56	5.95	3.39	4.41	0.55	8.65	5.73	5.47	4.77
C05	18.79	7.54	6.38	2.36	1.52	1.75	4.42	3.73	6.05	2.55	1.56	4.63	6.22
C06	22.97	6.17	5.22	7.50	8.59	5.25	5.44	3.05	11.55	7.64	8.86	3.79	7.67
C07	27.11	4.80	4.06	1.34	4.55	2.45	6.47	2.37	17.05	1.53	4.59	2.95	9.11
C08	31.32	3.43	2.90	6.47	0.51	4.55	7.50	1.70	2.38	6.62	0.52	2.11	10.56
C09	35.50	2.06	1.74	0.31	7.58	3.15	8.52	1.02	7.88	0.51	7.82	1.26	12.01
C10	39.68	0.67	0.58	5.44	3.54	3.85	9.55	0.34	13.38	5.60	3.65	0.42	13.45
P01	4.18	4.11	1.16	1.54	3.03	2.10	0.51	2.03	1.83	3.05	3.13	1.68	1.45
P02	6.26	3.43	1.74	2.57	2.52	1.05	1.03	1.70	4.58	1.53	2.61	0.84	2.17
P03	8.35	2.74	2.32	1.03	2.02	1.75	1.54	1.36	2.75	2.04	2.08	2.53	2.89
P04	10.44	2.06	2.90	3.08	1.52	0.70	2.05	1.02	5.50	2.55	1.56	1.26	3.62
P05	12.53	1.37	3.48	2.05	1.01	1.40	2.57	0.68	3.67	1.02	1.04	2.11	4.34

Table A.2

Retention time, dwell time, fragmentor voltage, collision energy, quantitative and qualitative ions of thirteen phenolic compounds related to LC-MS/MS method

Compounds	Rwtention time (min)	Dwell time (s)	Fragmentor voltage (V)	Collision energy (V)	$M\text{-}H^-$ (m/z)	Quantifier (m/z)	Qualifier (m/z)
Gallic acid	3.704	200	100	15	169	125	-[a]
Chlorogenic acid	4.030	200	100	10	353	191	-
Caffeic acid	4.742	200	100	15	179	135	-
p-Hydroxybenzoic acid	4.918	200	110	10	137	93	-
Vanillic acid	5.054	200	90	10	167	123	152
Ferulic acid	5.922	200	90	10	193	134	178
Resveratrol	6.506	200	110	15	227	143	185
Myricetin	7.468	200	110	25	317	151	179
Morin	9.124	200	110	20	301	125	151
Quercetin	12.108	200	110	20	301	151	179
Luteolin	14.226	200	110	30	285	133	175
Kaempferol	20.046	200	110	35	285	93	211
Apigenin	21.714	200	110	30	269	117	151

[a] Only one product ion is detected for quantification.

Table A.3

The quantitative results of thirteen phenolic compounds in five spiked prediction samples using LC-MS/MS method

Sample NO.	Predicted concentration (Mean value, n=3) ($\mu g\ mL^{-1}$)												
	GA	CA	CFA	p-HBA	VA	FA	RES	MY	MO	QU	LU	KA	AP
P01	4.89	4.03	1.29	1.15	2.44	2.18	0.54	1.97	1.54	3.03	3.00	1.64	1.36
	[0.32][a]	[0.20]	[0.17]	[0.07]	[0.23]	[0.17]	[0.05]	[0.07]	[0.27]	[0.11]	[0.11]	[0.05]	[0.07]
P02	6.15	3.41	1.76	2.22	1.86	1.06	1.17	1.65	4.33	1.49	2.43	0.80	2.02
	[0.29]	[0.14]	[0.18]	[0.25]	[0.31]	[0.14]	[0.14]	[0.04]	[0.26]	[0.08]	[0.10]	[0.02]	[0.13]
P03	8.57	2.55	2.49	0.74	1.59	1.83	1.61	1.25	2.42	1.90	1.99	2.37	2.64
	[0.81]	[0.17]	[0.27]	[0.11]	[0.12]	[0.17]	[0.23]	[0.03]	[0.25]	[0.13]	[0.06]	[0.14]	[0.12]
P04	11.33	2.01	3.08	2.89	1.47	0.68	1.97	1.01	5.37	2.53	1.42	1.11	3.49
	[0.21]	[0.15]	[0.41]	[0.06]	[0.10]	[0.06]	[0.08]	[0.07]	[0.21]	[0.08]	[0.10]	[0.17]	[0.17]
P05	11.99	1.14	3.26	2.06	1.00	1.43	2.31	0.57	3.58	0.96	0.93	2.01	4.35
	[0.21]	[0.07]	[0.12]	[0.11]	[0.06]	[0.06]	[0.17]	[0.04]	[0.17]	[0.04]	[0.02]	[0.07]	[0.02]
Recovery	83.2%[b]	89.8%	95.1%	87.4%	92.7%	90.4%	86.4%	78.2%	75.3%	81.2%	88.4%	73.0%	86.8%

[a] values in bracket represent standard deviation.

[b] Recovery is calculated as $(\sum_{n=1}^{N}(c_n - c_0)/\hat{c}_n)/N_P \times 100\%$, where c_n, c_0 are the prediction concentrations of analyte in *n*th spiked prediction sample and uspiked blank sample using LC-MS/MS method, respectively. Correspondingly, $\hat{c}_n$ is the actually spiked concentration in *n*th prediction sample.

Table A.4

The quantitative results of thirteen phenolic compounds (μg mL^{-1}) in nineteen wine samples of different vintage years using ATLD-assisted HPLC-DAD method, respectively

Wine sample	Vintage year	The contents of thirteen phenolic compouds												
		GA	CA	CFA	p-HBA	VA	FA	RES	MY	MO	QU	LU	KA	AP
1	2016	8.40	5.72	4.07	1.62	0.99	1.43	2.47	2.88	1.04	1.05	1.33	3.71	1.14
		[0.32][a]	[0.17]	[0.12]	[0.07]	[0.01]	[0.17]	[0.31]	[0.12]	[0.17]	[0.21]	[0.22]	[0.22]	[0.09]
2	2016	8.34	5.62	4.09	1.60	0.96	1.42	2.38	2.66	1.06	0.96	1.15	3.72	1.01
		[0.40]	[0.21]	[0.19]	[0.11]	[0.04]	[0.21]	[0.30]	[0.14]	[0.11]	[0.08]	[0.14]	[0.30]	[0.07]
3	2016	8.24	5.54	4.16	1.56	1.00	1.43	2.47	3.01	1.10	0.96	1.64	3.90	1.29
		[0.27]	[0.24]	[0.21]	[0.12]	[0.07]	[0.22]	[0.35]	[0.15]	[0.09]	[0.17]	[0.17]	[0.31]	[0.12]
4	2016	8.17	5.54	4.26	1.30	0.97	1.45	2.38	2.88	1.04	1.00	1.33	3.66	1.04
		[0.33]	[0.15]	[0.15]	[0.09]	[0.09]	[0.24]	[0.29]	[0.20]	[0.04]	[0.14]	[0.12]	[0.27]	[0.14]
5	2016	8.33	5.63	4.11	1.60	0.98	1.43	2.44	2.85	1.07	0.99	1.37	3.78	1.05
		[0.35]	[0.13]	[0.13]	[0.04]	[0.02]	[0.30]	[0.27]	[0.24]	[0.13]	[0.16]	[0.13]	[0.28]	[0.17]
6	2016	8.25	5.57	4.17	1.49	0.98	1.43	2.41	2.85	1.07	0.97	1.37	3.76	1.11
		[0.28]	[0.22]	[0.15]	[0.12]	[0.12]	[0.21]	[0.36]	[0.19]	[0.14]	[0.21]	[0.09]	[0.19]	[0.20]
7	2016	8.27	5.60	4.17	1.50	0.99	1.44	2.44	2.92	1.06	1.00	1.43	3.76	1.06
		[0.41]	[0.17]	[0.17]	[0.15]	[0.14]	[0.25]	[0.32	[0.14]	[0.17]	[0.15]	[0.11]	[0.31]	[0.21]
8	2015	8.31	5.12	4.30	1.49	1.10	1.03	2.56	2.90	0.98	1.43	0.83	3.26	1.44
		[0.36]	[0.15]	[0.23]	[0.02]	[0.03]	[0.27]	[0.31]	[0.16]	[0.07]	[0.02]	[0.05]	[0.29]	[0.25]
9	2015	8.60	5.13	4.36	1.43	1.06	1.00	2.43	2.95	1.02	1.00	0.88	3.21	1.20
		[0.30]	[0.20]	[0.24]	[0.13]	[0.05]	[0.19]	[0.30]	[0.11]	[0.04]	[0.08]	[0.07]	[0.34]	[0.19]
10	2015	8.63	5.30	4.23	1.17	1.19	1.00	2.40	2.99	0.85	0.83	0.94	3.18	1.64
		[0.19]	[0.16]	[0.18]	[0.03]	[0.09]	[0.15]	[0.27]	[0.21]	[0.09]	[0.12]	[0.10]	[0.25]	[0.16]
11	2015	8.45	5.35	3.95	1.27	1.48	1.01	2.53	2.88	0.93	0.99	1.03	3.28	1.09
		[0.43]	[0.14]	[0.25]	[0.11]	[0.12]	[0.21]	[0.29]	[0.12]	[0.05]	[0.16]	[0.09]	[0.21]	[0.13]
12	2015	8.31	5.31	4.03	1.17	1.70	1.01	3.24	3.09	1.15	1.02	1.03	3.17	1.09
		[0.21]	[0.18]	[0.14]	[0.14]	[0.10]	[0.17]	[0.25]	[0.25]	[0.08]	[0.21]	[0.05]	[0.24]	[0.27]
13	2014	7.87	5.12	4.14	1.00	1.00	0.92	2.63	2.50	1.42	1.00	1.06	3.35	1.37
		[0.25]	[0.19]	[0.25]	[0.10]	[0.11]	[0.20]	[0.35]	[0.21]	[0.12]	[0.20]	[0.04]	[0.30]	[0.18]
14	2014	7.99	4.99	4.25	1.07	1.09	0.91	2.65	2.52	1.51	0.91	0.97	3.36	1.36

		[0.28]	[0.22]	[0.17]	[0.13]	[0.13]	[0.23]	[0.33]	[0.17]	[0.14]	[0.14]	[0.06]	[0.17]	[0.25]
15	2014	7.90	5.02	4.09	0.98	1.39	0.93	2.77	2.64	1.74	1.03	1.17	3.46	1.48
		[0.30]	[0.11]	[0.13]	[0.15]	[0.17]	[0.26]	[0.35]	[0.19]	[0.15]	[0.17]	[0.15]	[0.24]	[0.21]
16	2014	7.76	5.13	4.21	0.84	1.53	0.94	2.64	2.55	1.55	0.99	1.00	3.34	1.22
		[0.23]	[0.24]	[0.12]	[0.19]	[0.14]	[0.17]	[0.37]	[0.22]	[0.17]	[0.15]	[0.11]	[0.31]	[0.20]
17	2014	8.06	5.14	4.73	1.44	0.85	0.93	2.53	2.39	1.32	1.89	0.94	3.33	1.25
		[0.30]	[0.26]	[0.24]	[0.18]	[0.09]	[0.28]	[0.39]	[0.24]	[0.13]	[0.13]	[0.12]	[0.34]	[0.27]
18	2014	8.08	5.17	4.70	1.36	1.03	0.94	2.76	2.34	1.35	1.26	0.81	3.39	1.29
		[0.34]	[0.23]	[0.26]	[0.12]	[0.07]	[0.18]	[0.22]	[0.23]	[0.11]	[0.22]	[0.15]	[0.24]	[0.31]
19	2014	8.11	5.18	4.77	1.52	1.36	0.93	3.08	2.40	1.26	1.10	0.91	3.33	1.39
		[0.33]	[0.15]	[0.17]	[0.11]	[0.05]	[0.20]	[0.27]	[0.24]	[0.08]	[0.20]	[0.09]	[0.19]	[0.25]

[a] Values in bracket represent standard deviation.

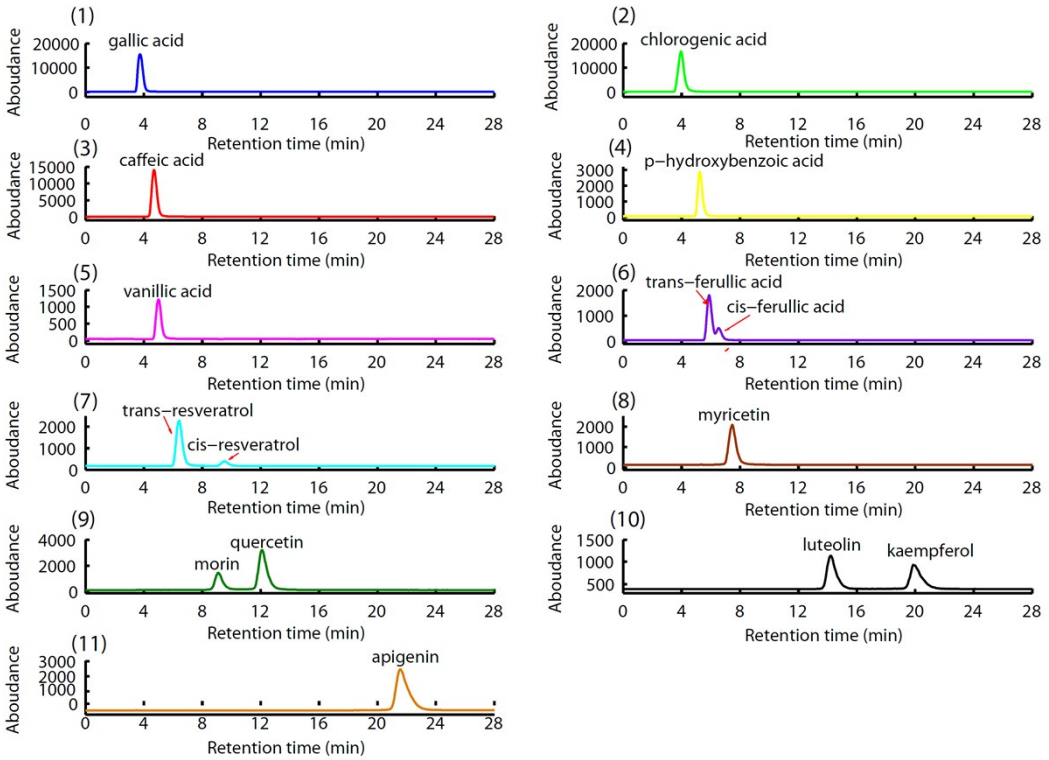

Figure A.1 Total ion chromatograms (TIC) of thirteen phenolic compounds in 6th calibration sample using LC-MS/MS in negative-ion multi-reaction monitoring (MRM) mode. concentration are as follows (in µg mL^{-1}): GA, 22.968; CA, 6.165; CFA, 5.220; p-HBA, 7.495; VA, 8.585; FA, 5.250; RES, 5.441; MY, 3.051; MO, 11.550; QU, 7.635; LU, 8.857; KA, 3,789; AP, 7.667. LC-separation was achieved on a ZORBAX Eclipse XDB-C18 reversed-phase column (3.5 µm, 150 mm × 2.1 mm i.d, Agilent) with a SB-C18 guard column (5 µm, 12.5 mm × 4.6 mm i.d., Agilent). An isocratic elution was performed in a period of 28.0 min at flow rate of 0.2 mL min^{-1} with two mobile phases: MeOH added 0.2% HCOOH (solvent A): H_2O added 0.2% HCOOH (solvent B), 30:70, (v/v).

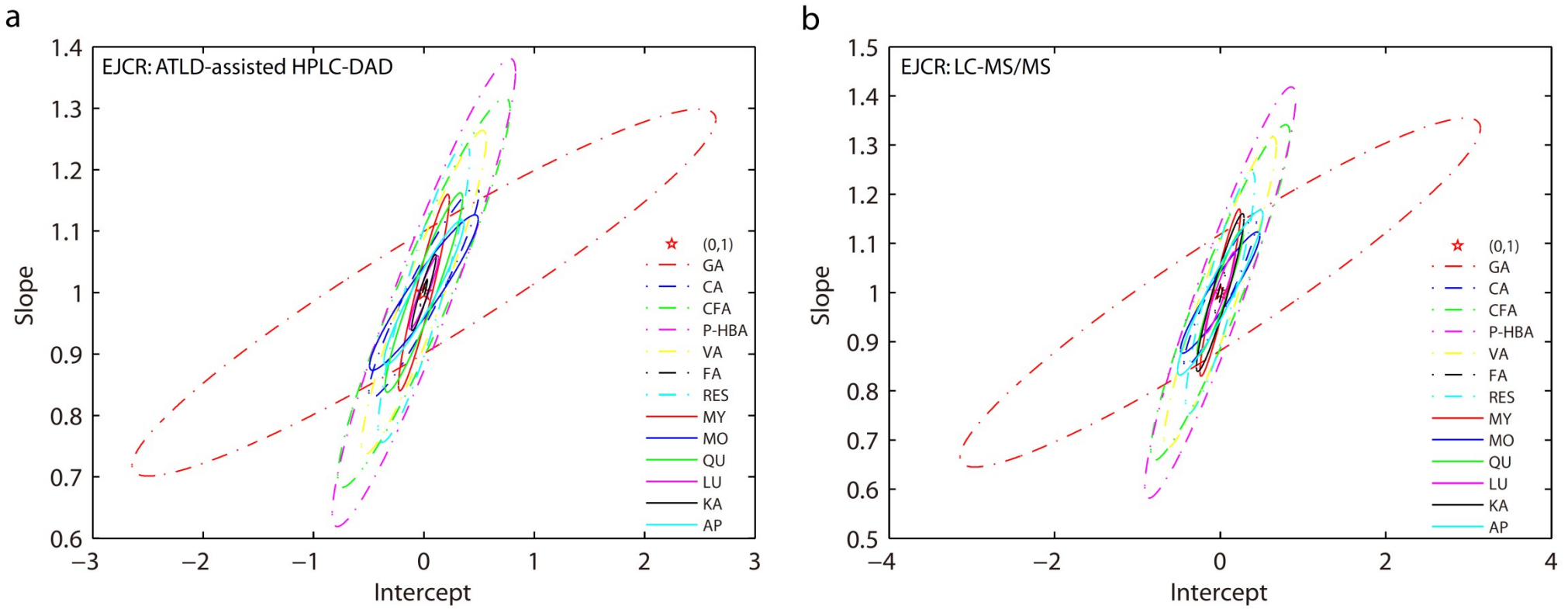

Figure A.2 The elliptical joint confidence regions (EJCRs)(at 95% confidence level) for the regression of the predicted against nominal concentrations of thirteen phenolic compounds in wine prediction samples using ATLD-assisted HPLC-DAD method and LC-MS/MS method, respectively. The red pentacle indicates the ideal point (0, 1) for intercept and slope.