Electronic Supplementary Information

Direct and Rapid Multi-Element Analysis of Wine Samples in Their Natural Liquid State by Laser Ablation ICPMS

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Contents

Table S1. Operating conditions and measurement parameters for the conventional SN-ICPMS analysis.

ICP-MS (Agilent 7700x)	
RF power	1400 W
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Carrier gas flow rate	0.75 L min^{-1}
Makeup gas flow rate	0.30 L min^{-1}
Sampling depth	14.0 mm
Sample uptake rates	100 μL min^{-1}
Integration time	0.3 s
Spray chamber	Scott double-pass type
Spray chamber temperature	2 ℃

Table S2. Relative signal intensities (mean±SD, n=5) of analytes in multi-element standard solutions with different ethanol concentrations (0%, 1%, 10% and 20% (v/v), respectively). The data were collected on two different days and analyzed under the same conditions cited in Table 1.

	Ethanol concentration (v/v)							
	Day 1				Day 2			
Analyte	**0%[a]**	**1%**	**10%**	**20%**	**0%[a]**	**1%**	**10%**	**20%**
Li	1.00±0.01	1.03±0.02	1.00±0.03	1.00±0.02	1.00±0.07	0.97±0.04	1.02±0.03	0.98±0.02
B	1.00±0.04	0.81±0.00	0.83±0.03	0.82±0.01	1.00±0.03	1.08±0.10	1.24±0.05	1.24±0.04
Mg	1.00±0.01	1.01±0.02	1.01±0.01	0.99±0.03	1.00±0.10	0.98±0.04	1.08±0.05	1.06±0.05
Al	1.00±0.02	1.02±0.04	1.05±0.03	1.05±0.03	1.00±0.04	0.98±0.03	1.07±0.03	1.04±0.02
V	1.00±0.02	1.01±0.02	1.00±0.02	1.00±0.02	1.00±0.02	1.01±0.02	1.00±0.02	1.00±0.02
Mn	1.00±0.02	1.01±0.02	1.00±0.02	0.99±0.02	1.00±0.03	1.00±0.03	1.00±0.02	1.02±0.02
Co	1.00±0.03	0.98±0.03	0.99±0.04	1.00±0.02	1.00±0.03	0.98±0.03	0.99±0.04	1.00±0.02
Cu	1.00±0.02	1.00±0.02	0.99±0.04	0.98±0.01	1.00±0.02	1.00±0.02	0.99±0.04	0.98±0.01
Zn	1.00±0.03	1.05±0.02	1.05±0.03	1.07±0.03	1.00±0.03	0.97±0.03	1.00±0.03	1.00±0.03
Rb	1.00±0.04	1.07±0.03	1.06±0.05	1.06±0.02	1.00±0.04	1.07±0.03	1.06±0.05	1.06±0.02
Sr	1.00±0.03	1.01±0.03	1.02±0.03	0.99±0.01	1.00±0.05	0.99±0.02	1.02±0.02	1.01±0.04
Y	1.00±0.03	1.03±0.01	0.98±0.02	0.99±0.02	1.00±0.04	0.98±0.03	1.01±0.03	1.01±0.02
Cs	1.00±0.01	1.05±0.04	1.03±0.02	1.03±0.01	1.00±0.05	0.97±0.02	0.97±0.02	0.97±0.03
Ba	1.00±0.02	1.02±0.02	1.00±0.03	1.01±0.02	1.00±0.02	0.98±0.03	1.02±0.03	1.02±0.02
La	1.00±0.02	1.00±0.02	1.00±0.02	0.98±0.03	1.00±0.04	1.01±0.03	1.05±0.05	1.05±0.04
Ce	1.00±0.02	0.99±0.01	0.99±0.03	0.98±0.01	1.00±0.03	0.97±0.03	0.99±0.03	1.00±0.02
Pr	1.00±0.01	0.99±0.02	1.00±0.02	0.98±0.01	1.00±0.04	0.97±0.03	1.01±0.02	1.01±0.02
Nd	1.00±0.01	1.01±0.01	1.01±0.03	1.02±0.02	1.00±0.05	0.95±0.03	0.97±0.04	0.98±0.01
Pb	1.00±0.01	1.00±0.01	1.01±0.02	1.00±0.03	1.00±0.02	0.93±0.03	0.97±0.03	0.96±0.02
U	1.00±0.02	1.00±0.03	0.99±0.02	0.98±0.02	1.00±0.01	0.98±0.03	1.00±0.02	1.02±0.04

[a] Signal intensities of all the analytes were referenced to In and normalized to that of the sample without ethanol addition (i.e., 0% ethanol concentration).

Table S3. Relative signal intensities (mean±SD, n=5) of analytes in in wine samples with different dilution factors (1, 1.25, 2, 2.5, and 5). Samples were analyzed under the conditions cited in Table 1.

	Dilution factor				
Analyte	**1[a]**	**1.25**	**2**	**2.5**	**5**
Li	1.00±0.05	0.92±0.03	1.00±0.05	1.01±0.07	1.05±0.11
B	1.00±0.04	0.98±0.05	1.02±0.03	1.03±0.07	0.98±0.07
Mg	1.00±0.02	1.03±0.12	1.08±0.06	1.11±0.04	1.11±0.09
Al	1.00±0.03	1.00±0.10	1.07±0.07	1.10±0.07	1.03±0.08
V	1.00±0.04	1.00±0.09	1.02±0.08	1.00±0.08	0.98±0.09
Mn	1.00±0.00	0.95±0.09	1.03±0.03	1.04±0.03	1.04±0.03
Co	1.00±0.10	0.94±0.14	1.04±0.20	1.03±0.16	1.03±0.29
Cu	1.00±0.05	0.94±0.07	0.99±0.02	1.02±0.03	1.03±0.04
Zn	1.00±0.01	0.98±0.05	1.01±0.01	1.01±0.02	0.98±0.06
Rb	1.00±0.01	0.97±0.04	1.00±0.02	1.01±0.03	1.01±0.03
Sr	1.00±0.01	0.98±0.04	1.01±0.01	1.01±0.02	1.03±0.04
Y	1.00±0.11	0.98±0.07	1.09±0.10	1.06±0.12	1.04±0.21
Cs	1.00±0.06	0.99±0.09	1.03±0.09	1.00±0.07	1.00±0.12
Ba	1.00±0.02	0.97±0.04	1.00±0.04	1.01±0.02	1.00±0.03
La	1.00±0.04	0.98±0.05	1.04±0.07	1.01±0.09	1.02±0.05
Ce	1.00±0.04	0.90±0.05	0.95±0.04	0.92±0.02	0.95±0.05
Pr	1.00±0.09	0.97±0.06	0.95±0.05	0.97±0.16	1.05±0.17
Nd	1.00±0.09	1.09±0.05	1.01±0.07	0.92±0.18	1.03±0.14
Pb	1.00±0.03	0.97±0.08	1.05±0.03	1.07±0.04	1.05±0.05
U	1.00±0.04	0.97±0.08	1.05±0.03	1.07±0.07	0.96±0.22

[a] Signal intensities of all analytes were referenced to In and normalized to that of the sample with a dilution factor of 1 (i.e., without dilution).

Table S4. Quantitative results calibrated by three different external standards: a multi-element standard solution (ST), a multi-element standard solution containing 10% ethanol (ST-10% ethanol), and NIST 610 glass. Samples were analyzed under the conditions cited in Table 1.

Element	Calibrated by ST **(ng mL^{-1})**	Calibrated by ST-10% ethanol **(ng mL^{-1})**	Calibrated by NIST 610 Glass **(ng mL^{-1})**
	(A)	(B)	(C)
Li	9.36	9.42	9.91
B[a]	12.1	11.1	10.4
Mg[a]	94.1	93.8	93.1
Al	500	498	485
V	25.0	25.4	26.0
Mn	731	735	744
Co	3.0	3.0	2.9
Cu	495	500	501
Zn	1224	1224	1880
Rb	664	677	645
Sr	629	645	607
Y	0.64	0.64	0.65
Cs	2.84	2.83	2.91
Ba	142	136	149
La	0.37	0.38	0.38
Ce	0.88	0.89	0.92
Pr	0.09	0.09	0.10
Nd	0.33	0.33	0.34
Pb	12.1	12.0	11.8
U	0.46	0.46	0.48

[a] values in μg mL^{-1}.

Table S5. Calculated t-values (t) for the comparison of elements concentrations obtained with LA-ICPMS in untreated wine samples and conventional SN-ICPMS in digested wine samples.

Element	W1	W2	W3	W4
Li	0.267	0.715	0.670	0.446
B	0.846	0.941	0.575	2.024
Mg	0.714	1.998	1.452	2.076
Al	2.020	2.086	1.783	2.066
V	2.084	0.133	0.710	0.382
Mn	1.098	1.525	0.889	0.296
Co	0.025	0.771	1.787	0.365
Cu	0.681	0.121	0.807	1.586
Zn	1.631	2.098	2.077	2.208
Rb	1.782	1.815	0.780	2.002
Sr	2.013	2.060	1.969	1.998
Y	0.511	0.262	0.272	1.226
Cs	2.149	1.331	0.401	0.820
Ba	1.450	1.446	1.472	0.264
La	0.163	1.592	1.164	0.028
Ce	0.446	0.364	1.417	0.249
Pr	0.300	0.411	0.014	1.074
Nd	0.780	0.150	0.190	1.621
Pb	0.593	1.339	0.033	0.580
U	0.083	1.182	0.588	1.572

* The critical t-value for 11 degrees of freedom and 95% confidence level: 2.201.

Equations employed to calculate t-values (t):

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\frac{S_p^2}{n_1} + \frac{S_p^2}{n_2}}}$$

$$S_p^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_1^2}{n_1 + n_2 - 2}$$

For degree of freedom (df): n_1=10, n_2=3, df=n_1+n_2-2.

* Since we obtained t-values lower than the critical t-value for 11 degrees of freedom (i.e., t<2.201), so we conclude that the differences of in the average concentrations obtained with between these two methods were is statistically insignificant at a 95% confidence level.

Table S6. Determined concentrations (mean±SD, ng mL^{-1}, except for B and Mg concentration) of 20 elements in two additional wine samples by LA-ICP-MS.

Element	W5-China (ng mL^{-1})	W6-Chile (ng mL^{-1})
	LA-ICP-MS (n = 10)	SN-ICP-MS (n = 10)
Li	80.8±3.7	7.15±0.20
B[a]	12.7±0.5	7.50±0.29
Mg[a]	146±4	120±1
Al	462±16	664±34
V	1.39±0.09	2.54±0.11
Mn	1331±45	1762±16
Co	3.4±0.2	4.5±0.1
Cu	263±10	52.1±0.6
Zn	340±12	901±5
Rb	813±24	4758±2
Sr	1673±58	972±7
Y	0.19±0.07	0.25±0.06
Cs	3.46±0.40	23.2±0.2
Ba	104±3	276±1
La	0.07±0.02	0.06±0.01
Ce	0.16±0.06	0.15±0.02
Pr	<LOD	0.02±0.01
Nd	<LOD	0.10±0.02
Pb	11.7±0.3	4.98±0.07
U	0.49±0.04	0.09±0.01

[a] values in μg mL^{-1}.

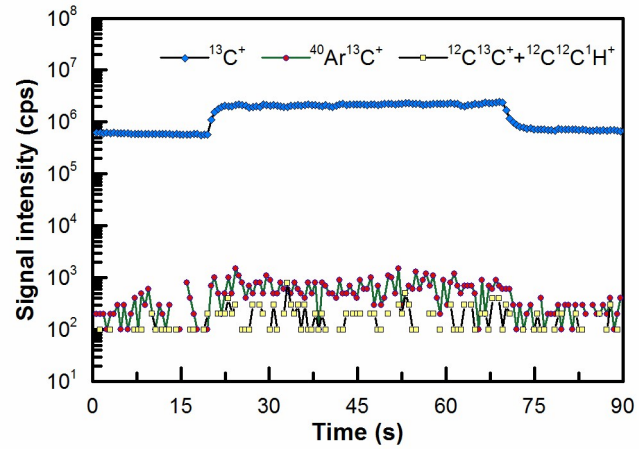

Fig. S1 Time-resolved signals of $^{13}C^+$, $^{40}Ar^{13}C^+$ and $^{12}C^{13}C^+ + ^{12}C^{12}C^1H^+$ in the LA-ICPMS analysis of a blank solution containing 10% (v/v) ethanol.

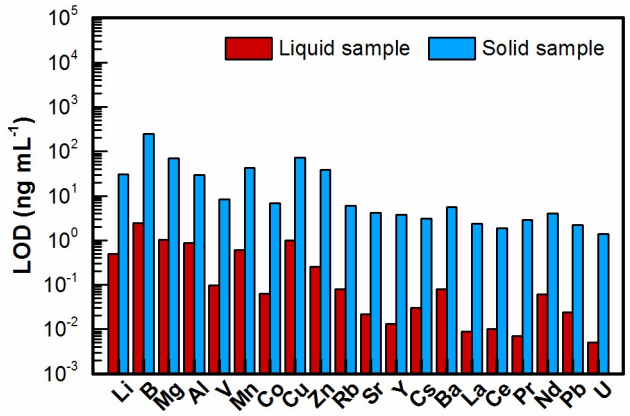

Fig. S2 Limits of detection (LOD) for 20 elements analyzed by LA-ICPMS in samples of liquid and solid states. Samples were analyzed with conditions cited in Table 1.

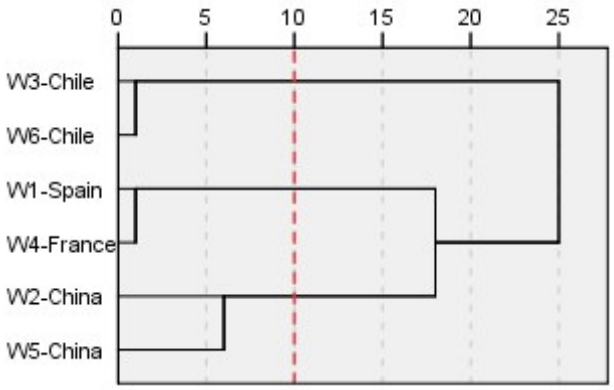

Fig. S3 Dendrogram for the cluster analysis of 20 elemental concentrations in six wine samples from four counties (Spain, China, Chile, France). The analysis was carried out on a SPSS 20.0 software.