Table S1. Calculated t-values and s-values for the comparison between the analytical results obtained by hTISIS/ICP-MS analysis under different operating conditions and by a reference method (microwave-assisted acid digestion and ICP-MS analysis using a conventional sample introduction system). Values of t lower than the critical *t-value* for 9 degrees of freedom and 95%-confidence level are highlighted in bold.

hTISIS T(ºC)	Mn						Mo						Pb					
	20 µL min⁻¹		30 µL min⁻¹		50 µL min⁻¹		20 µL min⁻¹		30 µL min⁻¹		50 µL min⁻¹		20 µL min⁻¹		30 µL min⁻¹		50 µL min⁻¹	
	t	s	t	s	t	s	t	s	t	s	t	s	t	s	t	s	t	S
50	16	62	22	52	13	66	3.0	1.3	21.8	0.6	22.0	0.6	12.4	0.6	**1.8**	0.5	**1.8**	0.7
75	10	57	14	46	18	50	10.0	1.0	16.4	0.7	20.6	0.6	8.2	0.8	**0.2**	0.6	4.6	0.5
100	3	59	5	53	7	55	14.3	0.7	6.6	0.7	13.1	0.7	13.9	0.7	3.5	0.8	**1.8**	0.6
125	**1.0**	151	**1.5**	73	**1.0**	93	4.1	0.8	**0.1**	1.1	**2.3**	0.8	8.1	0.6	**2.3**	0.6	**1.4**	0.6
150	**0.7**	69	**0.5**	51	3	61	8.1	0.9	**0.7**	0.7	2.7	0.7	11.1	1.0	4.7	0.5	**1.9**	0.6
200	11	95	6	148	6	109	4.5	0.9	**0.4**	0.7	4.1	0.7	13.4	1.0	4.1	0.8	**1.6**	0.6
300	10	60	16	50	12	66	21.7	0.7	5.2	0.8	8.3	0.7	**1.9**	0.6	4.1	0.6	5.7	0.5

Table S2. Calculated t values, degree of freedom (D.F.), the critical t value (95%-confidence level) and equations employed to calculate t and s. Values of t lower than the critical t-value level are highlighted in bold. Sample: Tempranillo 2.

		⁴⁷Ti	⁵¹V	⁵²Cr	⁵⁵Mn	⁵⁶Fe	⁶⁰Ni	⁶³Cu	⁶⁶Zn	⁷⁵As	⁹⁵Mo	¹¹¹Cd	¹⁴⁶Nd	¹⁴⁷Sm	¹⁵⁷Gd	¹⁵⁹Tb	²⁰⁸Pb
Conventional system	t[#]	**0.14**	NC	4.5	66	23.7	9.1	28	13	8.9	17	NC	NC	NC	NC	NC	64
	D.F.[$]	2	NC	2	3	2	2	2	2	2	2	NC	NC	NC	NC	NC	2
hTISIS	t[#]	7.2	NC	**4.1**	**0.94**	**2.2**	**1.0**	3.7	**1.8**	**4.3**	**1.4**	NC	NC	NC	NC	NC	8.3
	D.F.[$]	2	NC	2	6	4	2	2	2	2	2	NC	NC	NC	NC	NC	5

$$[\#]\ t=\frac{(\tilde{x}_1-\tilde{x}_2)}{\sqrt{\frac{s_1^2}{n_1}+\frac{s_2^2}{n_2}}} \qquad [\$]\ DF=\frac{\left(\frac{s_1^2}{n_1}+\frac{s_2^2}{n_2}\right)^2}{\left(\frac{s_1^4}{n_1^2(n_1-1)}+\frac{s_2^4}{n_2^2(n_2-1)}\right)}$$

; The F-test demonstrated that the variances of the procedures were not statistically comparable; NC: Not Calculated.

Table S3. Calculated t values, degree of freedom (D.F.), the critical t value (95%-confidence level) and equations employed to calculate t and s. Values of t lower than the critical t-value level are highlighted in bold. Sample: Gutturnio.

		⁴⁷Ti	⁵¹V	⁵²Cr	⁵⁵Mn	⁵⁶Fe	⁶⁰Ni	⁶³Cu	⁶⁶Zn	⁷⁵As	⁹⁵Mo	¹¹¹Cd	¹⁴⁶Nd	¹⁴⁷Sm	¹⁵⁷Gd	¹⁵⁹Tb	²⁰⁸Pb
Conventional system	t[#]	14	NC	**0.17**	10	**3.2**	98	150	17	**3.6**	44	NC	NC	NC	NC	NC	6.8
	D.F.[$]	5	NC	2	2	2	2	2	2	2	2	NC	NC	NC	NC	NC	3
hTISIS	t[#]	**2.5**	NC	**0.35**	**2.7**	**1.8**	9.2	130	**0.78**	**0.16**	**0.21**	NC	NC	NC	NC	NC	**4.2**
	D.F.[$]	5	NC	2	4	2	5	2	2	2	2	NC	NC	NC	NC	NC	2

$$[\#]\ t=\frac{(\tilde{x}_1-\tilde{x}_2)}{\sqrt{\frac{s_1^2}{n_1}+\frac{s_2^2}{n_2}}} \qquad [\$]\ DF=\frac{\left(\frac{s_1^2}{n_1}+\frac{s_2^2}{n_2}\right)^2}{\left(\frac{s_1^4}{n_1^2(n_1-1)}+\frac{s_2^4}{n_2^2(n_2-1)}\right)}$$

; The F-test demonstrated that the variances of the procedures were not statistically comparable; NC: Not Calculated.

Table S4. Calculated t values, degree of freedom (D.F.), the critical t value (95%-confidence level) and equations employed to calculate t and s. Values of t higher than the critical t-value level are highlighted in bold. Sample: Rioja.

		^{47}Ti	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{60}Ni	^{63}Cu	^{66}Zn	^{75}As	^{95}Mo	^{111}Cd	^{146}Nd	^{147}Sm	^{157}Gd	^{159}Tb	^{208}Pb
Conventional system	$t^{\#}$	**2.9**	NC	**1.1**	16	**2.5**	19	6.0	39	20	18	NC	NC	NC	NC	NC	6.6
	D.F.$^{\$}$	2	NC	2	4	2	2	2	3	2	2	NC	NC	NC	NC	NC	2
hTISIS	$t^{\#}$	**0.53**	NC	**0.40**	10	**0.41**	3.2	5.5	**1.5**	18	**3.7**	NC	NC	NC	NC	NC	**2.7**
	D.F.$^{\$}$	2	NC	2	4	2	2	2	2	2	2	NC	NC	NC	NC	NC	2

$$^{\#}t = \frac{(\bar{x}_1 - \tilde{x}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}; \quad ^{\$}DF = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\left(\frac{s_1^4}{n_1^2(n_1 - 1)} + \frac{s_2^4}{n_2^2(n_2 - 1)}\right)};$$

The F-test demonstrated that the variances of the procedures were not statistically comparable; NC: Not Calculated.

Table S5. Calculated slope, s_{Slope} and *t-values* for the temporal trends of QC data. Values of t higher than the critical t-value for 13 degrees of freedom and 95%-confidence level are highlighted in bold.

	^{47}Ti	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{60}Ni	^{63}Cu	^{66}Zn	^{75}As	^{95}Mo	^{111}Cd	^{146}Nd	^{147}Sm	^{157}Gd	^{159}Tb	^{208}Pb
slope	-0.0009	-0.037	-0.100	-0.002	-0.03	-0.044	-0.11	-0.011	-0.008	-0.00001	0.0005	0.00008	0.00010	0.0000	-0.0008	-0.039
s_{Slope}	0.0007	0.008	0.015	0.015	0.09	0.006	0.03	0.005	0.008	0.00003	0.0001	0.00009	0.00008	0.0002	0.0006	0.016
t	1.346	**4.749**	**6.783**	0.166	0.54	**6.754**	**3.99**	2.073	0.996	0.182	**4.780**	0.884	1.274	0.212	1.390	**2.460**