OPTIMIZATION AND VALIDATION OF A MICROWAVE DIGESTION METHOD FOR ANALYSIS OF ELEMENTS IN WINE USING ICP-MS

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Introduction

Red wine is a very complex mixture of ethanol and different organic compounds such as carbohydrates, organic acids, volatiles and bioactive compounds (anthocyanins, monomeric and polymeric flavan-3-ols, flavonols and phenolic acids). Therefore, sample pre-treatments are necessary for its multi-element analysis. Decomposition of organic matrix could be performed by wet digestion on a hot plate or in a microwave oven using concentrated HNO_3, $HClO_4$ and H_2SO_4 or mixtures of these acids.

✓In our study, the aim of the work was to develop, optimize and validate a microwave digestion method for wine sample pre-treatment, followed by ICP-MS determination of the elements.

Materials and Methods

Wine samples

Vranec wines from Tikveš region, R. Macedonia

Microwave digestion method

5 mL of wine was digested with 5 ml nitric acid (69.0%, *w/w*) and samples were made up to a final volume of 25 mL with ultrapure deionised water.

Microwave digestion system, Model MARS, CEM Corporation, USA) [1].

ICP-MS analysis

ICP-MS, model 7500cx, Agilent technologies

The concentration of 41 isotopes was measured in *No-gas* and *Helium* mode. The quality assurance of the method was approved with the standard addition method [1].

Results

✓Satisfactory linearity in all cases with correlation coefficients were obtained (R^2>0.99) (Table 1).

✓Method is accurate and convenient for quantitative analysis of elements in red and white wines. Satisfactory results for the recovery ranged between 83–120% (Table 2 and Table 3).

✓Satisfactory inter- and intra- day reproducibility. *RSD* values ranged from 0.32% to 15.1% for red wines and from 0.19% to 8.73% for white wine.

Table 1. Linear regression data

Element	Isotope	Unit	Slope	Intercept	R^2	LOD	LOQ
Ag	107	µg/L	0.0047	-0.0062	0.9996	0.023	0.077
Al	27	µg/L	1.037	10.67	0.9997	0.35	1.165
As	75	µg/L	0.009	0.0018	1.0000	0.0015	0.0049
B	11	µg/L	0.328	-8.980	0.9963	0.05	0.16
Ba	137	µg/L	0.013	-0.0098	0.9998	0.22	0.7326
Be	9	µg/L	0.0178	0.0017	0.9998	0.019	0.063
Bi	209	µg/L	0.00928	0.01046	0.9990	0.06	0.199
Ca	42	µg/L	0.00023	0.0398	0.9998	0.07	0.233
Cd	114	µg/L	0.0215	0.0241	0.9991	0.0056	0.019
Co	59	µg/L	1.376	-0.942	1.0000	0.00012	0.0004
Cr	53	µg/L	0.0074	-0.00534	0.9994	0.0052	0.017
Cu	63	µg/L	0.6148	6.970	0.9997	0.024	0.079
Fe	56	µg/L	1.368	150.5	0.9995	0.2961	0.976
Fe	57	µg/L	0.00172	0.0694	0.9999	1.23	4.095
Ga	69	µg/L	0.0551	-0.00164	0.9994	0.0095	0.031
Ge	72	µg/L	0.00025	0.00184	0.9993	0.0014	0.0046
In	115	µg/L	2.212	-2.311	0.9994	0.07	0.23
Li	7	µg/L	0.0595	0.0202	0.9997	0.0202	0.016
Mg	24	mg/L	187.2	67850	0.9993	0.0513	0.169
Mn	55	µg/L	1.676	-2.034	0.9991	0.0032	0.0106
Mo	95	µg/L	0.0000047	0.000313	1.0000	0.0012	0.0039
Na	23	µg/L	1.201	451.2	1.0000	0.0061	0.020
Ni	60	µg/L	0.0155	0.0037	1.0000	0.0015	0.0049
P	31	µg/L	0.0403	38.16	0.9977	0.055	0.18
Pb	206	µg/L	0.0231	0.0647	0.9988	0.011	0.037
Pb	207	µg/L	0.01977	0.0565	0.9995	0.027	0.089
Pb	208	µg/L	0.0480	0.1333	0.9991	0.032	0.106
Rb	85	µg/L	1.440	2.110	1.0000	0.41	1.36
S	34	µg/L	1.188	524	0.9996	0.022	0.073
Sb	121	µg/L	0.02892	13.67	0.9998	0.17	0.561
Se	77	µg/L	0.00084	0.000313	0.9990	0.00054	0.0018
Si	28	µg/L	0.5426	36.36	0.9994	0.060	0.198
Sn	120	µg/L	0.000052	0.004069	0.9970	0.0027	0.0089
Sr	88	µg/L	1.868	8.696	1.0000	0.00094	0.0031
Te	125	µg/L	0.03688	-0.00592	0.9998	0.033	0.11
Ti	48	µg/L	0.000659	-0.03982	0.9997	0.029	0.096
Tl	205	µg/L	1.867	-4.363	0.9995	0.00035	0.0012
V	51	µg/L	1.335	4.040	0.9999	0.00040	0.0013
Zn	66	µg/L	0.1922	2.269	0.9998	0.0018	0.0059

Table 2. Standard additions for checking accuracy of the digestion procedure

Element	Unit	Control wine	R (%)	Mean	SD	RSD (%)
Ag	µg/L	0.22	83.9	8.52	0.30	3.54
Al*	mg/L	0.24	85.9	1.10	0.11	9.76
As	µg/L	1.22	105	11.7	0.48	4.07
B	mg/L	3.39	121	4.65	0.25	5.41
Ba	mg/L	0.37	111	1.48	0.15	10.2
Be	µg/L	0.14	117	11.8	0.20	1.66
Bi*	µg/L	<LOQ	103	10.3	0.34	3.27
Ca**	mg/L	81.7	120	83.5	0.62	0.75
Cd*	µg/L	0.23	103	10.6	0.39	3.74
Co*	µg/L	2.2	117	13.9	0.34	2.47
Cr*	µg/L	0.016	102	10.2	0.36	3.54
Cu*	µg/L	0.027	112	11.2	0.55	4.89
Fe*	µg/L	0.62	98.6	10.5	0.27	2.54
Ga*	µg/L	11.5	121	23.6	0.48	2.03
Ge*	µg/L	0.06	100	10.1	0.51	5.06
In*	µg/L	<LOQ	117	11.7	0.44	3.77
Li*	µg/L	3.75	89.8	12.7	0.39	3.10
Mg**	mg/L	95.8	108	98.2	0.54	0.55
Mn**	mg/L	0.94	118	2.38	0.23	9.71
Mo*	µg/L	1.73	89.6	1.80	0.15	8.26
Na**	mg/L	5.87	86.3	6.73	0.37	5.50
Ni*	µg/L	20.1	120	32.1	0.67	2.07
P**	mg/L	135	119	136.2	0.62	0.46
Pb*	µg/L	4.16	115	15.7	0.48	3.08
Rb**	mg/L	3.91	90.0	4.81	0.36	7.46
S **	mg/L	78.5	120	79.7	0.83	1.05
Sb*	µg/L	0.30	87.1	9.01	0.35	3.90
Se*	µg/L	1.97	109	12.9	0.27	2.10
Si**	mg/L	15.9	120	17.1	0.30	1.75
Sn**	µg/L	1.02	94.6	10.5	0.28	2.66
Sr*	µg/L	0.61	90.6	9.67	0.36	3.74
Te*	µg/L	0.18	86.8	8.86	0.45	5.05
Ti*	µg/L	3.89	85.4	12.4	0.25	2.05
Tl*	µg/L	0.99	87.7	9.76	0.54	5.52
V*	µg/L	0.44	87.9	9.23	0.21	2.25
Zn*	µg/L	0.09	104	10.5	0.30	2.91

Table 3. Repeatability data (5 measurements per day with 3 injections per measurement)

Element	Unit	RED WINE		WHITE WINE	
		Mean concentration	RSD (%)	Mean concentration	RSD (%)
Ag	µg/L	2.55	2.70	27.2	6.13
Al	mg/L	0.66	8.45	1.23	2.45
As	µg/L	20.6	1.80	84.2	2.08
B	mg/L	2.53	2.43	2.46	1.27
Ba	µg/L	152	4.25	85.1	5.05
Be	µg/L	0.33	1.96	5.75	3.05
Bi	µg/L	42.8	1.68	36.0	1.88
Ca	mg/L	39.7	9.23	41.1	4.74
Cd	µg/L	0.0093	2.60	7.44	1.64
Co	µg/L	1.42	4.58	4.92	4.78
Cr	mg/L	0.46	8.73	1.39	1.62
Cu	µg/L	26.1	1.24	27.4	3.06
Fe	mg/L	1.23	3.45	1.52	1.87
Ga	µg/L	15.2	4.31	44.8	5.76
Ge	µg/L	0.0062	1.66	0.076	4.15
In	µg/L	6.03	4.38	231	1.29
Li	µg/L	4.86	1.08	4.41	1.16
Mg	mg/L	64.4	2.87	61.4	2.29
Mn	mg/L	0.75	2.14	0.86	2.24
Mo	µg/L	2.36	2.08	4.10	5.14
Na	mg/L	9.65	1.04	24.0	6.44
Ni	µg/L	19.2	6.28	32.4	11.8
P	mg/L	114	10.9	110	2.33
Pb	µg/L	12.4	1.07	25.2	10.7
Rb	mg/L	1.13	4.51	1.01	3.78
S	mg/L	74.3	8.53	95.3	2.83
Sb	µg/L	0.53	7.31	2.29	6.44
Se	µg/L	12.1	2.38	57.3	1.70
Si	mg/L	32.7	2.42	24.9	1.66
Sn	µg/L	5.15	1.73	4.89	3.21
Sr	µg/L	653	7.71	561	5.15
Te	µg/L	0.81	5.56	102	3.52
Ti	µg/L	21.7	4.63	26.1	4.96
Tl	µg/L	2.20	2.06	4.45	1.27
V	µg/L	12.2	4.95	56.8	1.53
Zn	µg/L	46.9	6.74	53.9	2.54

Table 4. Reproducibility for the analyzed elements in red and white wine (3 replicates×3 injections×3 days)

ELEMENT	Unit	RED WINE						WHITE WINE					
		Day 1	RSD (%)	Day 2	RSD (%)	Day 3	RSD (%)	Day 1	RSD (%)	Day 2	RSD (%)	Day 3	RSD (%)
Ag	µg/L	2.75	1.75	2.52	8.11	2.52	0.78	27.4	1.86	26.3	8.73	28.3	3.73
Al	mg/L	0.62	3.51	0.62	1.58	0.65	0.46	1.18	2.43	1.23	0.88	1.26	2.32
As	µg/L	24.5	3.43	22.2	6.24	16.3	3.18	79.6	0.86	82.0	8.38	83.8	6.25
B	mg/L	2.58	3.94	2.59	0.72	2.70	1.01	2.54	4.44	2.50	1.37	2.49	1.96
Ba	µg/L	151	1.48	154	4.21	151	3.81	89.1	2.40	92.8	1.39	84.7	0.88
Be	µg/L	0.40	7.25	0.34	5.41	0.39	12.7	5.80	4.99	6.12	4.59	6.21	3.11
Bi	µg/L	46.9	3.48	46.1	3.31	48.0	3.29	33.4	1.32	33.8	3.21	36.8	2.13
Ca	mg/L	37.0	1.19	38.1	3.83	39.3	1.18	40.5	3.17	42.0	2.47	40.5	2.49
Cd	µg/L	0.009	3.17	0.0092	2.81	0.0095	7.26	7.59	6.48	7.89	1.78	7.68	1.32
Co	µg/L	1.46	11.17	1.51	5.98	1.54	1.16	4.93	0.91	5.08	0.85	4.62	1.36
Cr	mg/L	0.47	1.64	0.46	1.79	0.40	3.30	0.42	2.02	0.41	0.54	0.42	1.32
Cu	µg/L	28.9	0.85	27.4	2.11	26.36	0.33	27.5	2.07	28.0	0.19	27.2	2.48
Fe	mg/L	1.31	1.91	1.33	0.79	1.34	7.96	1.51	8.57	1.56	6.31	1.51	2.48
Ga	µg/L	12.06	1.92	15.6	1.70	12.49	1.05	45.8	2.73	47.4	3.33	43.2	3.19
Ge	µg/L	0.006	0.74	0.0061	11.9	0.0065	3.02	0.077	1.57	0.074	1.24	0.078	1.17
In	µg/L	6.05	3.03	6.07	5.24	5.94	1.89	231	1.77	217	3.58	228	3.44
Li	µg/L	4.80	2.79	4.97	2.99	5.17	2.45	4.33	1.41	4.80	1.78	4.46	2.89
Mg	mg/L	62.1	3.14	63.5	1.85	65.8	1.11	61.7	1.17	62.9	3.03	62.6	2.91
Mn	mg/L	0.76	0.93	0.76	1.61	0.78	6.35	0.82	6.44	0.84	1.02	0.85	2.24
Mo	µg/L	2.46	6.76	2.35	3.83	2.50	0.74	3.48	0.50	3.62	1.21	3.79	2.91
Na	mg/L	9.53	2.78	9.68	1.28	10.1	0.92	21.0	3.87	20.2	2.15	22.0	1.93
Ni	µg/L	19.8	1.91	19.5	1.81	20.3	5.75	30.7	0.38	32.9	2.08	33.7	6.04
P	mg/L	114	3.27	120	1.55	113	2.81	109	5.63	107	1.79	111	3.71
Pb	µg/L	12.0	3.11	12.3	1.99	12.4	1.88	25.0	1.12	25.5	1.68	23.6	1.33
Rb	mg/L	1.12	8.73	1.13	2.4	1.16	8.47	0.94	5.16	0.95	2.67	1.10	6.63
S	mg/L	70.6	4.92	73.5	1.5	79.1	2.82	90.7	4.61	92.2	0.85	91.4	1.87
Sb	µg/L	0.55	3.51	0.52	7.69	0.56	1.61	2.47	2.02	2.61	3.35	2.14	1.87
Se	µg/L	13.3	1.53	12.5	5.59	10.1	15.1	53.1	2.07	53.8	2.11	52.6	4.58
Si	mg/L	32.5	2.16	33.6	0.32	29.9	3.07	23.9	4.74	23.6	0.81	23.4	3.09
Sn	µg/L	5.11	4.17	5.10	10.9	5.03	12.8	5.51	1.47	4.13	4.46	4.87	1.23
Sr	µg/L	642	3.09	651	0.54	665	12.3	507	5.21	522	1.23	517	2.54
Te	µg/L	0.67	7.52	0.86	1.54	0.67	3.09	93.7	7.82	99.1	3.37	96.9	0.81
Ti	µg/L	21.6	2.03	21.9	1.75	22.8	0.81	24.2	1.47	25.3	2.75	26.1	0.72
Tl	µg/L	0.23	2.43	2.30	0.69	2.39	1.38	4.00	5.33	4.05	1.59	4.31	2.07
V	µg/L	19.2	3.87	12.5	0.56	19.9	1.88	53.9	2.81	55.9	1.94	53.0	0.50
Zn	µg/L	56.5	2.50	48.1	0.69	54.0	0.77	55.7	1.23	54.3	2.45	56.9	1.42

Conclusion

Fast and accurate method for sample preparation followed with ICP-MS for multi-element analysis of wine was optimized and developed. The method presented satisfactory linearly, LOD, LOQ, accuracy, repeatability and reproducibility for total 38 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, In, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Rb, S, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V, Zn). It was then used for determination of the elements content in Vranec wines.

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