

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 HNO₃, HClO₄ and H₂SO₄ 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].

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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	0.00023	-0.01046	0.9995	0.06	0.19
Al	27	µg/L	1.037	10.67	0.9997	0.35	1.15
As	75	µg/L	0.009	-0.0018	0.9999	0.015	0.049
B	11	µg/L	0.328	-8.980	0.9963	0.05	0.16
Ba	137	µg/L	0.113	-0.0098	0.9998	0.22	0.736
Be	9	µg/L	0.0178	0.017	0.9998	0.019	0.063
Bi	209	µg/L	0.00028	-0.01046	0.9995	0.06	0.19
Ca	42	µg/L	0.00023	-0.01046	0.9998	0.07	0.23
Ca	114	µg/L	0.00023	-0.01046	0.9998	0.07	0.23
Co	59	µg/L	1.376	-0.942	1.0000	0.00012	0.0004
Cr	53	µg/L	0.0103	-0.0013	0.9999	0.0052	0.016
Cu	63	µg/L	0.4348	6.970	0.9997	0.024	0.079
Fe	56	µg/L	0.365	-130.5	0.9995	0.2961	0.93
Fe	57	µg/L	0.00172	0.0048	0.9999	1.23	4.095
Ga	69	µg/L	0.00023	-0.01046	0.9998	0.07	0.23
Ge	73	µg/L	0.00023	-0.01046	0.9998	0.07	0.23
Ge	115	µg/L	0.00023	-0.01046	0.9998	0.07	0.23
Li	7	µg/L	0.0595	0.0020	0.9997	0.0022	0.016
Mg	24	µg/L	197.2	1762.0	0.9993	0.0019	0.006
Mn	55	µg/L	1.676	-2.034	0.9991	0.0032	0.0106
Mn	95	µg/L	0.0000007	0.0000007	0.9999	0.0000007	0.0000007
Mn	23	µg/L	1.201	43.2	1.0000	0.0061	0.020
P	31	µg/L	0.0403	38.16	0.9977	0.003	0.18
Pb	206	µg/L	0.01035	-0.0007	0.9999	0.011	0.039
Pb	207	µg/L	0.01977	0.0562	0.9995	0.027	0.089
Pb	208	µg/L	0.01035	-0.0007	0.9999	0.011	0.039
Rb	85	µg/L	1.440	2.110	1.0000	0.41	1.36
Rb	84	µg/L	1.18	1.998	0.9998	0.022	0.073
Sb	121	µg/L	0.02892	13.67	0.9998	0.17	0.51
Sb	77	µg/L	0.0004	-0.00013	0.9990	0.0004	0.018
Sb	28	µg/L	45.626	36.36	0.9994	0.060	0.186
Sr	120	µg/L	0.00052	-0.00409	0.9997	0.0027	0.0089
Sr	88	µg/L	0.00059	-0.0009	1.0000	0.00094	0.0031
Te	125	µg/L	0.03688	-0.00592	0.9999	0.033	0.11
Ti	48	µg/L	0.00069	0.0002	0.9997	0.0007	0.0023
Ti	205	µg/L	1.867	-4.363	0.9995	0.00003	0.0012
V	51	µg/L	0.1325	0.040	0.9999	0.00060	0.0020
Zn	66	µg/L	0.1922	2.269	0.9998	0.0018	0.0059

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	µg/L	0.66	8.45	123	4.43
As	µg/L	20.6	1.80	84.2	2.08
B	µg/L	152	4.25	85.1	5.05
Ba	µg/L	63.9	1.96	87.9	3.68
Be	µg/L	42.8	1.68	38.0	1.88
Bi	µg/L	39.7	9.23	41.1	4.74
Ca	µg/L	0.0003	2.60	7.44	1.64
Ca	µg/L	0.0003	2.60	4.92	4.79
Co	µg/L	0.46	8.73	1.59	1.62
Cr	µg/L	0.61	1.24	27.4	0.66
Cu	µg/L	1.23	3.45	1.72	1.87
Fe	µg/L	15.2	4.31	44.8	4.4
Ge	µg/L	0.0002	1.66	0.0002	1.15
Ge	µg/L	0.0002	1.66	0.0002	1.15
Li	µg/L	4.86	1.04	4.41	1.16
Mg	µg/L	6.05	2.98	64.9	1.29
Mn	µg/L	0.75	2.18	0.86	2.34
Mn	µg/L	0.75	2.18	0.86	2.34
Ni	µg/L	0.65	1.04	24.0	6.44
P	µg/L	12.1	2.38	32.4	4.14
Pb	µg/L	1.14	10.9	1.0	2.33
Pb	µg/L	1.14	10.9	1.0	2.33
Rb	µg/L	1.13	4.21	1.01	3.78
Rb	µg/L	1.13	4.21	1.01	3.78
Sb	µg/L	0.23	7.51	2.09	6.44
Sb	µg/L	0.23	7.51	2.09	6.44
Sr	µg/L	32.7	2.42	24.0	1.66
Sr	µg/L	32.7	2.42	24.0	1.66
Ti	µg/L	65.3	7.71	56.1	5.15
Ti	µg/L	65.3	7.71	56.1	5.15
Ti	µg/L	21.7	4.63	36.1	4.96
Ti	µg/L	21.7	4.63	36.1	4.96
V	µg/L	12.2	4.96	56.8	1.33
V	µg/L	12.2	4.96	56.8	1.33
Zn	µg/L	46.6	6.74	33	2.54

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

Element	Unit	Control	R (%)	Mean	RSD (%)	
Ag	µg/L	0.22	83.9	8.52	0.30	3.54
Al	µg/L	0.24	82.6	11.20	0.11	97.2
As	µg/L	1.22	105	11.7	0.48	4.07
B	µg/L	3.39	121	4.65	0.25	8.41
Ba	µg/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	4.00	103	10.3	0.34	3.77
Bi	µg/L	4.00	103	10.3	0.34	3.77
Ca	µg/L	0.23	103	10.6	0.39	3.74
Ca	µg/L	0.23	103	10.6	0.39	3.74
Co	µg/L	0.027	112	11.9	0.25	8.49
Co	µg/L	0.027	112	11.9	0.25	8.49
Cu	µg/L	0.016	102	10.2	0.36	3.54
Cu	µg/L	0.016	102	10.2	0.36	3.54
Fe	µg/L	0.62	98.6	10.5	0.27	2.54
Fe	µg/L	0.62	98.6	10.5	0.27	2.54
Ge	µg/L	0.06	100	10.1	0.51	5.06
Ge	µg/L	0.06	100	10.1	0.51	5.06
Li	µg/L	4.00	117	11.7	0.44	3.77
Li	µg/L	4.00	117	11.7	0.44	3.77
Mg	µg/L	95.8	108	98.2	0.54	0.55
Mg	µg/L	95.8	108	98.2	0.54	0.55
Mn	µg/L	1.73	89.6	1.80	0.15	8.26
Mn	µg/L	1.73	89.6	1.80	0.15	8.26
Ni	µg/L	20.1	120	32.1	0.67	2.07
Ni	µg/L	20.1	120	32.1	0.67	2.07
Pb	µg/L	0.30	87.1	9.01	0.25	3.96
Pb	µg/L	0.30	87.1	9.01	0.25	3.96
Pb	µg/L	4.16	115	15.7	0.48	3.08
Pb	µg/L	4.16	115	15.7	0.48	3.08
Rb	µg/L	79.5	120	79.7	0.83	1.05
Rb	µg/L	79.5	120	79.7	0.83	1.05
Sb	µg/L	1.97	109	12.9	0.27	1.19
Sb	µg/L	1.97	109	12.9	0.27	1.19
Sr	µg/L	15.9	120	12.1	0.30	1.72
Sr	µg/L	15.9	120	12.1	0.30	1.72
Ti	µg/L	1.89	88.8	8.86	0.45	5.05
Ti	µg/L	1.89	88.8	8.86	0.45	5.05
Ti	µg/L	3.89	85.4	12.4	0.25	2.05
Ti	µg/L	3.89	85.4	12.4	0.25	2.05
V	µg/L	0.44	87.9	0.23	0.21	2.25
V	µg/L	0.44	87.9	0.23	0.21	2.25
Zn	µg/L	100	94	10	0.30	2.41

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

Element	Unit	RED WINE			WHITE WINE		
		Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
Ag	µg/L	2.75	2.52	2.11	25.2	27.4	26.3
Al	µg/L	0.62	1.53	0.62	1.58	0.45	1.18
Al	µg/L	0.62	1.53	0.62	1.58	0.45	1.18
As	µg/L	28.1	18.4	22.2	6.05	18.6	1.23
As	µg/L	28.1	18.4	22.2	6.05	18.6	1.23
B	µg/L	258	304	259	0.72	0.70	1.01
B	µg/L	258	304	259	0.72	0.70	1.01
Ba	µg/L	10.40	7.25	10.34	5.41	10.39	12.7
Ba	µg/L	10.40	7.25	10.34	5.41	10.39	12.7
Be	µg/L	46.91	34.81	46.61	33.81	48.89	33.90
Be	µg/L	46.91	34.81	46.61	33.81	48.89	33.90
Ca	µg/L	37.89	1.19	38.81	3.83	39.3	1.18
Ca	µg/L	37.89	1.19	38.81	3.83	39.3	1.18
Co	µg/L	0.0089	0.317	0.0089	0.383	0.0095	0.266
Co	µg/L	0.0089	0.317	0.0089	0.383	0.0095	0.266
Cu	µg/L	1.46	111.17	1.51	1.98	1.54	1.16
Cu	µg/L	1.46	111.17	1.51	1.98	1.54	1.16
Fe	µg/L	0.047	1.64	0.46	1.79	0.40	1.30
Fe	µg/L	0.047	1.64	0.46	1.79	0.40	1.30
Ge	µg/L	0.81	0.85	0.74	1.11	0.63	0.51
Ge	µg/L	0.81	0.85	0.74	1.11	0.63	0.51
Li	µg/L	1.31	1.91	1.33	0.79	1.34	7.96
Li	µg/L	1.31	1.91	1.33	0.79	1.34	7.96
Mg	µg/L	120.60	13.02	135.03	120.49	13.05	145.81
Mg	µg/L	120.60	13.02	135.03	120.49	13.05	145.81
Ni	µg/L	15.006	16.74	0.0061	31.9	0.0066	3.02
Ni	µg/L	15.006	16.74	0.0061	31.9	0.0066	3.02
Pb	µg/L	0.005	0.008	0.007	0.024	0.019	0.21
Pb	µg/L	0.005	0.008	0.007	0.024	0.019	0.21
Rb	µg/L	62.1	3.14	63.8	1.85	66.8	1.11
Rb	µg/L	62.1	3.14	63.8	1.85	66.8	1.11
Sb							