

METHOD DEVELOPMENT FOR MEASUREMENT OF ELEMENTS IN HUNGARIAN RED WINES BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY (ICP-OES)

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ICP-OES (inductively coupled plasma optical emission spectrometry) was used to determine the element content of red wines. Development of the method involves various procedures of sample handling as well as repeatability and reproducibility measurements. Measurements were made for the following 16 elements: Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn. The relative standard deviation of repeatability ranged from 0.41% (potassium) to 27% (cadmium) and that of reproducibility varied between 0.73% (boron) to 52% (cobalt). Recovery of the elements was determined by standard addition with results ranging from 90.6% (phosphorus) to 116.2% (boron). After that, 15 red wine samples were measured. Significant differences were found in the Al, B, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn ($P < 0.001$) concentration of wine samples. Correlation studies revealed parallel changes in phosphorus-potassium, phosphorus-magnesium and zinc-manganese concentrations ($r = 0.857, 0.875, 0.838$). According to principal component analysis, measurements of zinc-, sodium-, boron-, copper- and strontium content gave almost the same results as obtained with 16 different elements. According to a two dimensional non-linear map of absolute values of principal component analysis, wines from Szekszárd and Eger could be differentiated, whereas the analysis of wines from Villány, the Mátra Mountains and Lake Balaton showed overlapping results.

Keywords: red wine, metal ion (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn) content

Wine is a very popular drink in all parts of the world. The metal content of wine has a great impact on the quality, and since cloudiness and precipitation depend on element concentration, determination and monitoring of the element content of wine is of special significance. Cloudiness and precipitation may appear during wine-making or months after bottling. Some of the metal compounds known to be responsible for this

unfavourable effect are: calcium tartarate, potassium tartarate, calcium phosphate, iron tannate or phosphate, copper – protein and copper sulphide (OUGH et al., 1982). The unfavourable flavour of wine may also be due to high zinc, magnesium, sodium and potassium content (LÓPEZ-ARTIGEZ et al., 1996). Some elements, e.g. lead, aluminum, contaminate wine in a secondary process, in the course of wine-making (ESCHNAUER & SCOLLARY, 1995; HERNÁNDEZ et al., 1996).

Various methods have been applied to determine the mineral element content of wines, e.g.: spectrophotometry (KUMAR et al., 1991), flame emission spectrometry (LIMA et al., 1991), anodic stripping voltametry (ANTUNES & SIMAO, 1993; HERRERO et al., 1994), potentiometric stripping analysis (OSTAPCZUK, 1993), adsorptive voltametry (BEBEKI & VOULGARPOULOS, 1992), atomic absorption spectrometry (BALUJA-SANTOS & GONZALEZ-PORTAL, 1992; CACHO et al., 1992), graphite furnace atomic absorption spectrometry (LARROQUE et al., 1994; CABRERA-VIQUE et al., 1997), electrothermal atomic absorption spectrometry (ALMEIDA et al., 1992; MATTHEWS & PARSONS, 1993; ALMEIDA et al., 1994), X-ray fluorescent analysis (HASWELL & WALMSLEY, 1998), inductively coupled plasma atomic emission spectrometry (GALLI & ODDO, 1992; BÓDYNÉ SZALKAI & FODOR, 1996; THIEL & DANZER, 1997) and inductively coupled plasma mass spectrometry (STROH et al., 1994; GREENOUGH et al., 1997).

In our investigations, the element content of wine was determined by ICP-OES. Owing to the lack of reference material on wine, authenticity measurements were carried out, and after verifying the correctness of the method, 15 red wine samples were examined. Evaluation of the samples was made by statistical analysis: calculation of significance, correlation studies, one way analysis of variance (ANOVA) and principal component analysis (PCA). Multivariate mathematical-statistical methods, e.g. PCA (MARDIA et al., 1979), are often used to extract maximum information from data matrices of considerable dimension. A benefit of the PCA method is that it offers a lot of information with a reduce of variables. PCA is also suitable both for the calculation of two-two variable relationships, and for simultaneous study of relationships between all variables. This technique can also be used for transforming the original set of variables into a new set of uncorrelated ones. These ‘principal components’ are closed to the original variables and are arranged in a decreasing order of variance (CHATFIELD & COLLINS, 1980). Although PCA renders the original data dimensionless, it may occasionally give multidimensional matrices of PC loadings and PC variables. As the capacity of the human brain is limited in the evaluation of data distributed in multidimensional space, the matrices of PC loadings and variables are usually reduced to two or three dimensional values by non-linear mapping techniques, which allows graphical presentation of these values in a two-dimensional plane or three-dimensional space.

The aim of this study was to develop a method for the element measurement of metal concentration in wine samples and to determine the difference in the element content of red wines according to type and origin.

1. Materials and methods

1.1. Instrument

For the determination of elements a sequential ICP-OES (inductively coupled plasma optical emission spectrometer), type Atom Scan 25 was applied. In parallel measurements the following elements were determined: Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Sr, Zn. The parameters of measurements are summarized in Table 1. The detection limit is equal to the values given by Thermo Jarrell Ash. Standard solutions (prepared from Merck ICP standards) were in the same matrix as in the samples. In the case of Sample preparation method 1, the standard solutions contained 1.1% alcohol; for Sample preparation method 2 the standard solutions were diluted only with deionized water, and in the rest of sample preparation methods standard solutions were HNO₃ (5%). Three times 3 s integration time, blank subtraction and background correction were applied.

The wine sample used for verifying the correctness of the method was: Nagyrédei Cabernet Franc, half dry red wine, a 1997 vintage (0.75 l) with 11% (v/v) alcohol content, bottled by Szőlőskert Co-operative, Nagyréde, Hungary. After verification of the method, 15 commercially available Hungarian red wine samples were analyzed (Table 2).

1.2. Sample preparation method

Three parallel preparations were made for each sample preparation method.

1./ The wine sample diluted (ten fold) with deionized water was vaporized into the plasma without sample preparation.

2./ Alcohol was evaporated from the wine (25 ml), which was diluted with deionized water to 25 ml.

3./ Alcohol was evaporated from the wine (25 ml), and after the addition of HNO₃ (5 ml, 65%), the solution was diluted with deionized water to 25 ml.

4./ The wine sample (25 ml) was concentrated to dry matter, then digested with HNO₃ (5 ml). After digestion the sample was diluted with deionized water to 25 ml.

5./ The wine sample (25 ml) was concentrated to dry matter, then digested with a mixture of HNO₃ and H₂O₂ (5 ml + 2 ml). After digestion the sample was diluted with deionized water to 25 ml.

Table 1

Parameters of the element measurements and the calibration data for ICP

Element	Wavelength (nm)	Plasma power (W)	Detection limit (mg l ⁻¹)	Upper concentration applied (mg l ⁻¹)	Slope	Y-intercept	Correlation coefficient of regression line
Al	396.152	1350	0.020	10	1.53147	-0.019603	0.9992
B	249.773	1350	0.002	10	2.53891	-0.80208	0.9987
Ba	455.403	1150	0.001	10	0.048398	-0.001300	0.9996
Ca	393.366	950	0.0005	10	2.62714	-0.46115	0.9965
Cd	226.502	1750	0.002	2	2.65581	-0.091891	0.9995
Co	228.616	1550	0.003	2	1.85300	0.000741	0.9991
Cr	267.716	1750	0.004	2	3.04692	0.009141	0.9990
Cu	324.754	1150	0.002	2	0.382800	-0.007426	0.9853
Fe	259.940	1750	0.002	20	1.31272	-0.004988	0.9966
K	766.490	1150	0.100	100	112.192	-2.70007	0.9998
Mg	279.553	1150	0.0005	50	1.95402	-0.058230	0.9999
Mn	257.610	1150	0.001	5	0.249651	-0.000533	0.9980
Na	589.592	1150	0.010	5	2.24296	-2.29694	0.9818
P	185.943	1350	0.060	35	38.6742	0.011028	0.9984
Sr	407.771	1150	0.0005	2	0.034014	-0.017325	0.9987
Zn	206.200	1350	0.002	2	2.26586	-0.11707	0.9981

For further measurements (repeatability, reproducibility and recovery) Sample preparation method 5 was chosen.

1.3. Repeatability

After digestion only one sample was obtained by Sample preparation method 5, which was measured four times a day for a period of four days.

1.4. Reproducibility

Four sample preparations (Sample preparation method 5) were carried out for four days. Each sample was measured four times a day.

1.5. Recovery

For the determination of element recovery, standard addition was used: known amounts of standard solutions were added to the wine samples, then the solution was sampled as usual (Sample preparation method 5).

Table 2

Wine samples examined

Sample numbers	Wines
1	Villányi Kékoportó, 1996 (Villányi Borászati Rt)
2	Egri Bikavér, 1996 (Hunyadvin Rt)
3	Villányi Cuvée, 1996 (Roth József, Villány)
4	Szekszárdi Kékfrankos, 1996 (Hungarovin)
5	Szekszárdi Vörös Kékfrankos, 1997 (Balatonvin Kft)
6	Tihanyi Kékfrankos, 1996 (Badacsonyi Pincegazdaság)
7	B-B Cabernet Sauvignon, 1995 (Balatonboglári Borgazdasági Rt)
8	Kékoportó Villányi, 1996 (Balatonvin Kft)
9	Szekszárdi Merlot, 1995 (Hungarovin Rt)
10	Mátraaljai Kékfrankos, 1996 (Hungarovin Rt)
11	Pinot Noir, 1996 (Balatonvin Kft)
12	Dél-Baltoni Merlot, 1996 (Balatonboglári Borgazdasági Rt)
13	Villányi Cabernet Sauvignon, 1996 (Balatonvin Kft)
14	Boglári Kékfrankos, 1996 (Balatonboglári Borgazdasági Rt)
15	Tihanyi Cabernet Franc, 1996 (Badacsonyi Pincegazdaság)

1.6. Statistical analysis

Mean values and standard deviations (SD) were calculated from the results. For comparison of the mean values, one way analysis of variance (ANOVA) was applied. Correlation coefficients were calculated on the basis of the Pearson theory (HAVLICEK & CRAIN, 1988). Principal component analysis was used to transform the original – possibly multicollinear – variables into independent ones. The variables were measured elements, while the observed values were taken from red wine samples. The relationships were presented by two-dimensional non-linear mapping.

2. Results

The concentration ranges of elements were determined. As, Hg, Li, Mo, Pb, V, Ti, Ni, Sn and Sb content was found to be below the detection limit, therefore, no authenticity measurements for these elements could be performed.

Linearity of the calibration curves was evaluated by analysing standard solutions (aqueous- HNO₃, 5%) with concentrations ranging from 0 to 50 mg l⁻¹. Calibration parameters for ICP are shown in Table 1.

The effect of sample handling on the measurement was monitored by different preparation procedures. As can be seen in Table 3, the first sample preparation procedure gives different results for element concentration than obtained by the other

preparation procedures. The P value was <0.05 for aluminum, boron, barium, calcium, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, phosphorus, sodium, strontium and zinc. Since the wine sample could not be nebulized to the plasma, the sample was diluted to ten times its original volume with deionized water. Therefore, the concentration of some elements was below the detection limit. The second sampling also shows differences in element concentration related to the third, fourth and fifth sample preparation method, particularly for barium, copper, phosphorus and zinc as can also be seen in Table 3. In the second sample preparation method, organic compounds in the wine were not digested. Organic compounds proved to increase the intensity of barium, copper and zinc, while in the case of phosphorus a decrease in intensity could be observed. The 3rd, 4th and 5th sample preparation method did not show significant differences for most elements (Al, B, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Sr).

For the study of repeatability the same sample solution was measured four times a day throughout four days. Mean values and standard deviations were calculated for each day. No significant difference was found (except for Na) between the mean values of daily measurements (Table 4). Relative standard deviations varied from 0.41% (K) to 27% (Cd). Of these data, the measurements of cadmium and chromium showed high relative standard deviation (above 5%) owing to their low concentration. Sodium measurement also showed high RSD as reported by other authors as well (LOPEZ-ARTIGEZ et al., 1996).

For the study of reproducibility, Sample preparation method 5 was daily applied. Relative standard deviation was found to be somewhat higher than observed for repeatability measurements (Table 4). Unfortunately, the results obtained by cobalt and sodium measurements cannot be considered reliable.

For the recovery measurements, standard addition was used for each element. The standard solution was added to the wine sample and then digested as usual. Recovery data are also given in Table 4. As may be seen, mean recovery is 102.2%, from which the recovery of elements ranges between 90.6% (phosphorus) and 116.2% (boron).

After validation of the sample preparation method, 15 red wine samples were analysed (Table 5). Element concentrations in wines show significant differences ($P<0.001$) for Al, B, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn. Relatively high concentration of potassium, magnesium, phosphorus and sodium can be observed in Villányi Kékoportó (1996). Similarly, high element concentration was measured by OUGH and co-workers (1982) for potassium, magnesium, sodium, and by THIEL and DANZER (1997) for phosphorus.

Correlation studies show parallel changes in the phosphorus-potassium ($r=0.857$), phosphorus-magnesium ($r=0.875$) and zinc-manganese ($r=0.838$) concentration of wines (Fig. 1).

Table 3
Element concentration and \pm SD (mg l^{-1}) of red wine sample according to different sample handling and the P value for 3d, 4th, 5th sample preparation method

Elements	1	2	3	4	5	P value
Al	0.258 ± 0.011	1.137 ± 0.026	1.149 ± 0.081	1.152 ± 0.075	1.143 ± 0.022	>0.8 ns
B	2.258 ± 0.028	4.460 ± 0.061	4.593 ± 0.356	4.629 ± 0.336	4.959 ± 0.104	0.1756 ns
Ba	<0.005	0.1414 ± 0.0013	0.1361 ± 0.0042	0.1347 ± 0.0028	0.136 ± 0.001	0.0597 sig.
Ca	84.29 ± 0.34	86.08 ± 1.50	89.27 ± 2.24	90.17 ± 3.16	89.21 ± 0.80	0.1722 ns
Cd	<0.02	0.0280 ± 0.0012	0.0229 ± 0.0068	0.0206 ± 0.0078	0.017 ± 0.002	0.1581 ns
Co	<0.03	0.0365 ± 0.0061	0.0371 ± 0.0058	0.0318 ± 0.0058	0.0283 ± 0.0098	0.4778 ns
Cr	<0.04	0.0308 ± 0.0068	0.0269 ± 0.0074	0.0246 ± 0.0087	0.024 ± 0.005	0.6573 ns
Cu	0.0750 ± 0.0021	0.0896 ± 0.0044	0.0773 ± 0.0067	0.0710 ± 0.0080	0.069 ± 0.008	0.0254 sig.
Fe	2.898 ± 0.027	3.500 ± 0.034	3.429 ± 0.075	3.441 ± 0.059	3.489 ± 0.077	0.4787 ns
K	944.8 ± 10.2	912.4 ± 21.2	927.5 ± 14.8	939.4 ± 13.9	928.0 ± 12.6	0.3012 ns
Mg	95.99 ± 1.34	102.82 ± 1.05	96.70 ± 8.39	103.32 ± 2.91	99.45 ± 0.85	0.2837 ns
Mn	0.831 ± 0.008	1.001 ± 0.011	0.9638 ± 0.0260	0.9684 ± 0.0187	0.991 ± 0.020	0.1364 ns
Na	14.53 ± 0.17	50.59 ± 0.91	52.78 ± 12.76	54.22 ± 14.00	55.84 ± 1.12	0.1582 ns
P	102.5 ± 2.5	129.8 ± 0.9	138.7 ± 5.3	136.6 ± 4.4	123.4 ± 3.0	0.0043 sig.
Sr	0.828 ± 0.004	0.760 ± 0.006	0.719 ± 0.029	0.719 ± 0.029	0.747 ± 0.020	0.1178 ns
Zn	0.0714 ± 0.0115	0.3053 ± 0.0057	0.2644 ± 0.0560	0.2463 ± 0.0293	0.251 ± 0.008	0.0570 sig.

1 without any preparation, 2 alcohol was evaporated, 3 alcohol was evaporated then HNO_3 was added, 4 concentrated to dry matter then digested with HNO_3 , 5 concentrated to dry matter then digested with a mixture of HNO_3 and H_2O_2

Table 4

The statistical data of repeatability, reproducibility (mean element concentration and standard deviation in $\mu\text{g L}^{-1}$, relative standard deviation in %) and the results of recovery study in %

Elements	Repeatability			Reproducibility			Recovery		
	Mean	SD (RSD)	P	F	Mean	SD (RSD)	P	F	Recovery
Al	1.130	0.021 (1.86)	0.4308	0.989	1.174	0.011 (0.94)	0.7100	0.468	100.6
B	4.873	0.065 (1.33)	0.3669	1.55	4.780	0.085 (0.73)	0.6615	0.544	116.2
Ba	0.137	0.002 (1.09)	0.2401	1.60	0.138	0.003 (2.17)	0.05	5.124	99.8
Ca	89.32	0.004 (1.01)	0.5434	0.749	92.43	0.98 (1.06)	0.2034	1.786	98.8
Cd	0.020	0.005 (27)	>0.8	0.284	0.010	0.001 (7.77)	>0.8	0.184	101.6
Co	0.024	0.006 (2.34)	0.4616	0.918	0.005	0.003 (52)	0.2822	1.431	102.2
Cr	0.028	0.003 (10.4)	0.4070	1.05	0.294	0.001 (2.38)	>0.8	0.217	104.2
Cu	0.073	0.004 (4.93)	0.5317	0.772	0.081	0.002 (2.22)	0.5553	0.727	104.2
Fe	3.468	0.044 (1.27)	0.4308	0.989	3.779	0.037 (0.98)	0.4078	1.046	99.4
K	924.6	3.8 (0.41)	>0.8	0.058	999.5	13.08 (1.31)	0.1083	2.509	116.2
Mg	99.95	0.46 (0.46)	0.7845	0.358	101.1	0.9 (0.89)	0.2259	1.671	97.5
Mn	0.987	0.006 (0.61)	>0.8	0.084	10.28	0.019 (1.85)	0.1103	2.488	98.3
Ns	35.15	2.29 (6.51)	0.0009	11.0	40.02	7.95 (19.88)	<0.0001	49.76	113.0
P	125.0	1.1 (0.88)	0.7897	0.350	135.6	1.90 (1.40)	0.0875	4.325	90.6
Sr	0.738	0.014 (1.90)	0.1875	1.88	0.717	0.015 (2.09)	0.1645	2.023	102.5
Zn	0.253	0.005 (1.19)	>0.8	0.087	0.260	0.007 (2.69)	0.2892	1.405	94.6

Table 5
Element concentration of different wine samples and \pm standard deviation in $\log t^d$

Elements	Villányi Kékorpató, 1996	Egri Bikavér, 1996	Villányi Cuvée, 1996	Szekszárdi Kékfrankos, 1996	Szekszárdi Vörös Kékfrankos, 1997
Al	6.53 \pm 0.04	3.01 \pm 0.05	2.43 \pm 0.04	4.60 \pm 0.05	4.51 \pm 0.05
B	7.42 \pm 0.20	6.58 \pm 0.02	6.31 \pm 0.129	6.28 \pm 0.20	4.82 \pm 0.103
Ba	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Ca	7.84 \pm 0.22	71.90 \pm 0.74	31.63 \pm 0.28	72.28 \pm 1.24	71.59 \pm 0.65
Cd	<0.002	<0.002	<0.002	<0.002	<0.002
Co	0.099 \pm 0.011	0.045 \pm 0.065	0.066 \pm 0.054	<0.003	<0.003
Cr	0.102 \pm 0.014	0.078 \pm 0.022	0.061 \pm 0.0065	0.086 \pm 0.030	0.117 \pm 0.044
Cu	0.0318 \pm 0.0016	0.0338 \pm 0.0001	0.2146 \pm 0.0015	0.0187 \pm 0.0009	0.1624 \pm 0.0025
Fe	7.85 \pm 0.28	3.82 \pm 0.04	15.25 \pm 0.30	4.53 \pm 0.08	7.44 \pm 0.16
K	1528 \pm 54	744.23 \pm 6.09	1029 \pm 20	708.9 \pm 4.2	1057 \pm 10
Mg	188.24 \pm 3.27	75.63 \pm 2.14	71.54 \pm 0.91	77.56 \pm 1.78	55.78 \pm 1.55
Mn	0.362 \pm 0.013	0.138 \pm 0.002	0.293 \pm 0.004	0.126 \pm 0.004	0.270 \pm 0.005
Na	45.80 \pm 2.71	17.79 \pm 1.81	18.14 \pm 1.30	25.12 \pm 1.45	18.5 \pm 1.2
P	340.22 \pm 7.05	88.95 \pm 2.39	133.5 \pm 2.1	95.4 \pm 2.5	127.8 \pm 1.7
Sr	0.0036 \pm 0.0003	0.0160 \pm 0.0001	0.0090 \pm 0.0004	0.0110 \pm 0.0001	0.0085 \pm 0.0005
Zn	1.842 \pm 0.049	0.225 \pm 0.0105	1.340 \pm 0.020	0.262 \pm 0.024	0.547 \pm 0.031

Continued Table 5

Elements	Tihanyi Kékfrankos, 1996	B-B Cabernet Savignon, 1995	Károlyi Villány, 1996	Szekszárdi Merlot, 1995	Matraaljai Kékfrankos, 1996
Al	9.77 ± 0.11	2.42 ± 0.04	5.08 ± 0.09	2.70 ± 0.08	3.08 ± 0.03
B	4.70 ± 0.14	7.82 ± 0.07	5.19 ± 0.05	7.89 ± 0.11	9.21 ± 0.15
Ba	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Ca	58.14 ± 0.83	39.77 ± 0.44	74.22 ± 0.57	80.02 ± 3.20	16.27 ± 0.28
Cd	<0.002	<0.002	<0.002	<0.002	<0.002
Co	0.012 ± 0.008	0.087 ± 0.033	<0.003	<0.003	<0.003
Cr	0.1363 ± 0.0251	0.0352 ± 0.0126	0.2078 ± 0.059	0.0515 ± 0.0056	0.0698 ± 0.0191
Cu	0.1069 ± 0.0005	0.0978 ± 0.001	0.1911 ± 0.0017	0.0413 ± 0.0015	0.0299 ± 0.0016
Fe	5.38 ± 0.041	4.305 ± 0.114	9.13 ± 0.06	3.31 ± 0.01	4.52 ± 0.08
K	743.5 ± 11.7	814.7 ± 14.9	1099 ± 5	877.1 ± 17.0	690.9 ± 15.8
Mg	59.40 ± 0.5	83.89 ± 1.18	57.50 ± 1.5	90.98 ± 0.29	81.98 ± 2.03
Mn	0.035 ± 0.001	0.217 ± 0.004	0.296 ± 0.002	0.074 ± 0.0020	0.162 ± 0.004
Ni	18.82 ± 1.29	16.89 ± 0.99	24.21 ± 0.49	13.23 ± 0.86	9.6 ± 0.9
P	80.6 ± 2.7	107.5 ± 1.8	129.9 ± 3.7	98.31 ± 0.99	90.69 ± 1.24
Sr	0.0985 ± 0.0005	0.0208 ± 0.0005	<0.0005	0.0125 ± 0.0002	0.0119 ± 0.0006
Zn	0.160 ± 0.031	0.476 ± 0.021	0.621 ± 0.028	0.157 ± 0.012	0.322 ± 0.010

Continued Table 5

Elements	Pinot Noir, 1996	Del-Balansoni Merlot, 1996	Villányi Cabernet Sauvignon, 1996	Boglári Kékfrankos, 1996	Tihanyi Cabernet Franc, 1996
Al	3.26 ± 0.04	2.95 ± 0.06	3.03 ± 0.03	5.72 ± 0.07	2.53 ± 0.04
B	4.54 ± 0.09	6.17 ± 0.09	6.33 ± 0.05	6.94 ± 0.01	7.78 ± 0.06
Ba	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Ca	19.86 ± 0.26	77.71 ± 1.02	10.83 ± 0.07	14.42 ± 0.23	27.05 ± 0.23
Cd	<0.002	<0.002	<0.002	<0.002	<0.002
Co	<0.003	0.085 ± 0.063	0.126 ± 0.072	0.108 ± 0.054	<0.003
Cr	0.0896 ± 0.0089	0.6574 ± 0.0231	0.6924 ± 0.0180	0.6970 ± 0.0274	0.1087 ± 0.0161
Cu	0.0679 ± 0.0008	0.2413 ± 0.0031	0.6607 ± 0.0018	0.1347 ± 0.0022	0.0745 ± 0.0017
Fe	9.81 ± 0.15	5.53 ± 0.09	5.29 ± 0.11	3.78 ± 0.13	5.24 ± 0.04
K	1.35 ± 31	700.7 ± 17.0	794.7 ± 11.6	788.6 ± 31.6	712.0 ± 18.0
Mg	68.81 ± 1.23	61.99 ± 0.53	67.88 ± 1.22	89.50 ± 0.61	90.06 ± 0.76
Mn	0.338 ± 0.003	0.347 ± 0.002	0.260 ± 0.003	0.368 ± 0.001	0.087 ± 0.001
Na	12.46 ± 1.87	16.93 ± 0.64	4.7 ± 0.41	4.17 ± 1.68	12.52 ± 0.60
P	115.8 ± 1.4	93.4 ± 0.2	70.0 ± 1.17	127.2 ± 1.6	96.72 ± 0.19
Sr	0.0043 ± 0.0008	0.0164 ± 0.0008	0.0121 ± 0.0003	0.0100 ± 0.0007	0.0201 ± 0.0003
Zn	2.359 ± 0.036	1.181 ± 0.021	0.815 ± 0.026	1.557 ± 0.016	0.355 ± 0.008

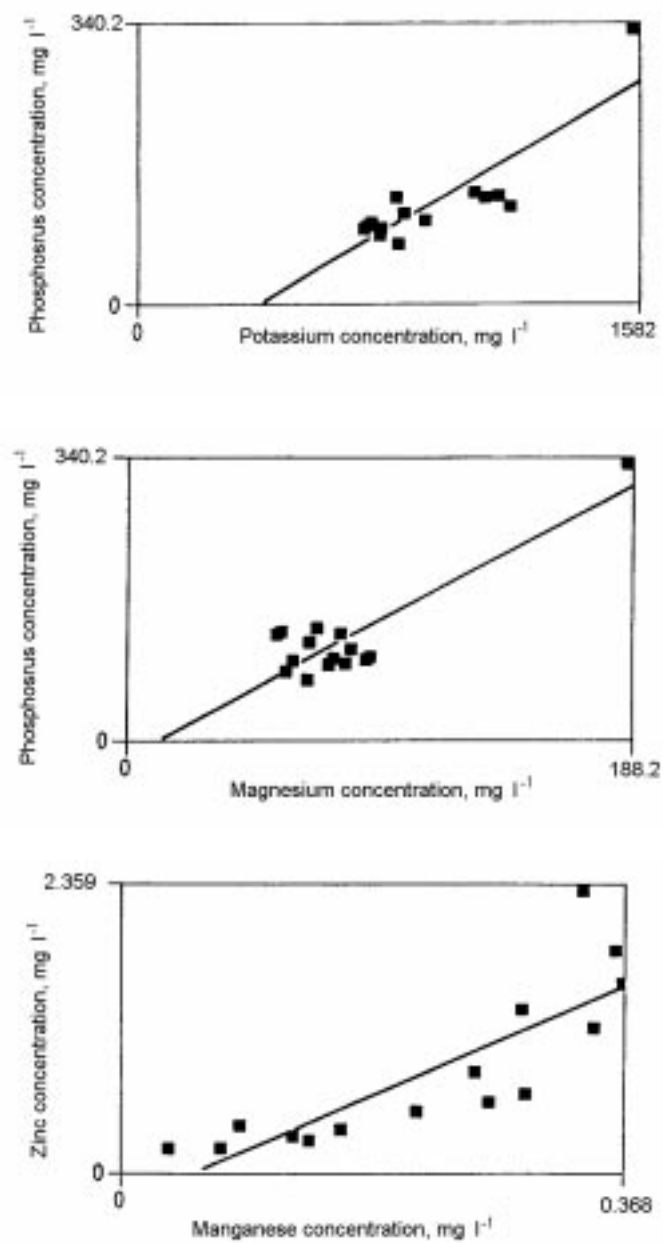


Fig. 1. Parallel changes of a. phosphorus and potassium, b. phosphorus and magnesium, c. zinc and manganese concentrations

One way analysis of variance was used for the comparison of wines on the basis of origin and type. No significant difference was found in wines originating from the region of Lake Balaton and other areas. The result was the same, when the variance between "Villányi", "Szekszárdi" and "Balatoni" wines was calculated. The variance in Kékoportó, Kékfrankos, Cabernet and Merlot was significant for potassium and strontium ($P < 0.05$). Since this method of statistical analysis did not prove to be suitable for the exact differentiation of wines, probably due to the insufficient number of wine samples, therefore, further investigations are required.

The results of PCA are given in Table 6. Eighty-eight percent of the total variance may be attributed to six principal components. These results indicate that 16 elements can be substituted as variables by five background (imaginary) variables with only 16.54% loss of total information. The principal component analysis does not prove, only indicates mathematically the existence of these background-variables as measurable parameters, which means that the measurement of five appropriately chosen elements is sufficient to obtain the same information. Most of the elements have high loadings ($>|0.5|$) in the first PC component, which shows that these parameters greatly affect the element-composition of red wines: calcium, cobalt, potassium, magnesium, manganese, phosphorus and zinc. Sodium has high loadings in the second; aluminium, boron, chromium and iron have high loadings in the third; copper in the fourth and strontium in the fifth PC component. On the basis of highest PC loadings, the elements most characteristic of red wines are zinc, sodium, boron, copper and strontium, however, according to the validation method, the results obtained for sodium cannot not be evaluated.

The two-dimensional non-linear map (NLM) of absolute values of PCA loadings is shown in Fig. 2. The elements are divided into five different clusters. Each cluster contains the elements given above. According to the PC variables by NLM (Fig. 3), the red wines studied are divided into five clusters, according to origin. The wines from Szekszárd and Eger can be differentiated according to PCA results on the basis of measured elements while the wine clusters from Villány, the Mátra Mountains and Lake Balaton give overlapping results and therefore, cannot be differentiated by this analytical method.

Table 6

Relationship between the origin of red wines and their element content. Results of principal component analysis, principal component variables and loadings (calculated from correlation matrix)

	Eigenvalues	Explained variance		Cumulative values	
I	6.7335	33.67%		33.67%	
II	3.3275	16.64%		50.31%	
III	3.1050	15.52%		65.83%	
IV	1.9985	9.99%		75.82%	
V	1.5279	7.64%		83.46%	

Wines	Principal component variables (scores)				
	I	II	III	IV	V
Villányi Kékoportó	7.0739	4.1277	0.3365	0.1810	0.1650
Egri Bikavér	-1.6551	0.3586	0.9458	-0.6977	-0.8607
Villányi Cuvée	0.6394	-0.8268	-0.9428	2.3101	-1.8894
Szekszárdi Kékfrankos	-2.4484	1.7063	0.1392	-0.8502	-1.0057
Szekszárdi Vörös Kékfrankos	-2.2612	1.6978	-2.5865	0.6052	-0.6054
Tihanyi Kékfrankos	-1.5403	1.2375	-1.8622	-2.6718	0.7749
B-B Cabernet Sauvignon	-0.6747	-0.1023	1.8348	0.1585	-1.8238
Kékoportó Villányi	-0.5501	-0.9067	-3.5365	0.0501	1.5364
Szekszárdi Merlot	-2.9319	1.3845	2.2885	2.5440	2.7048
Mátraaljai Kékfrankos	0.1091	-0.8358	2.6489	-1.7093	0.4813
Pinot Noir (Villányi)	2.5798	-1.8883	-1.2244	0.1077	-0.0581
Dél-Balaton Merlot	-0.9627	-0.7516	-0.1156	1.7241	-0.03654
Villányi Cabernet Sauvignon	0.9347	-2.4508	0.6587	-0.6568	-0.3456
Boglári Kékfrankos	2.8878	-2.7968	0.3072	-0.0683	1.2580
Tihanyi Cabernet Franc	-1.2002	0.0467	0.01084	-1.0266	0.0338

Elements	Principal component loadings				
	I	II	III	IV	V
Al	0.2315	0.3416	-0.4856	-0.4767	0.3326
B	0.0917	0.0735	0.8857	0.0262	0.0774
Ca	-0.7637	0.2982	-0.2862	0.2471	0.1243
Co	0.5486	-0.2554	0.2272	0.2015	-0.2690
Cr	0.0510	0.0268	-0.7471	-0.3697	0.3872
Cu	-0.3207	-0.0198	-0.1317	0.7237	0.5246
Fe	0.4534	-0.2766	-0.5336	0.3671	-0.1875
K	0.6749	0.4044	-0.3887	0.3118	0.0538
Mg	0.6962	0.5891	0.3532	0.0555	0.0729
Mn	0.6758	-0.3001	-0.3202	0.4101	-0.1582
Na	0.3666	0.8368	0.0892	0.0549	-0.3100
P	0.7756	0.5671	-0.0941	0.1793	0.0238
Sr	-0.3526	0.1468	0.5013	0.4879	0.5147
Zn	0.8055	-0.2392	-0.2265	0.3086	-0.0932

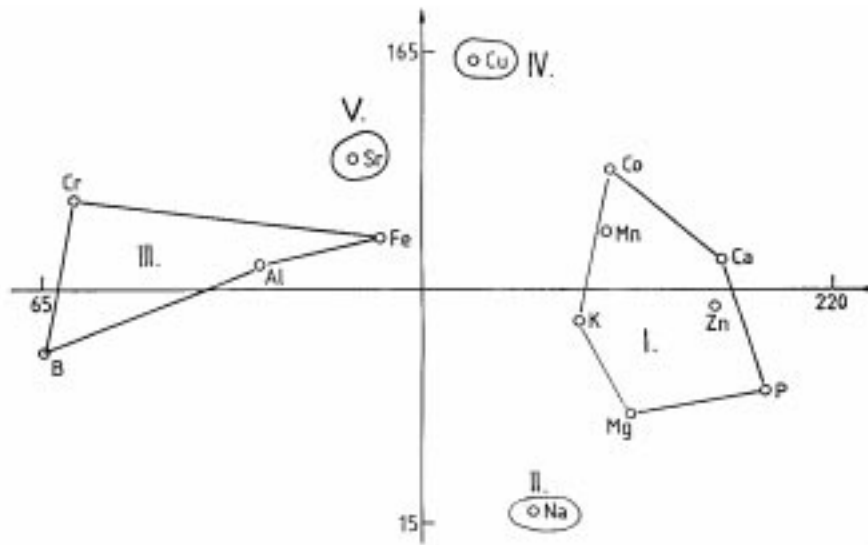


Fig. 2. The two dimensional non-linear map of absolute values of principal component analysis

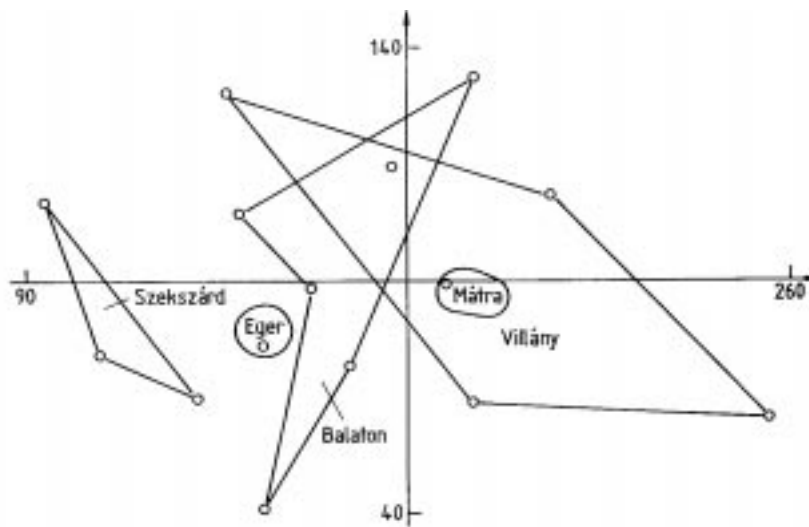


Fig. 3. Representation of principal component variables by a non-linear map

3. Conclusion

Owing to the effect of organic compounds on the intensity of elements, decomposition of these compounds is required prior to ICP-OES. After digestion, the sample preparation methods did not show significant differences in the concentration of aluminum, boron, calcium, cadmium, cobalt, chromium, iron, potassium, magnesium, manganese and strontium. The study of repeatability showed high relative standard deviation (above 5%) in the cadmium, sodium and chromium content. In the study of reproducibility, the results obtained for cobalt and sodium cannot be considered reliable.

According to the statistical analysis, the zinc, boron, copper and strontium content of Hungarian red wines gave almost the same results as obtained by the measurement of 16 different elements. On the basis of PCA results, the wines from Szekszárd and Eger can be differentiated on the basis of their measured elements while the analyses of wine clusters from Villány, the Mátra Mountains and Lake Balaton show overlapping results. Consequently, latter wines cannot be differentiated by principal component analysis. Naturally, these results refer only to the 15 commercial wines examined. Further investigations with more wine samples are required for the exact differentiation of wines according to origin or type.

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