Analysis of trace elements and major components in wine with the Thermo Scientific iCAP 7400 ICP-OES

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Key Words

Authenticity, Major Components, Provenance, Trace Elements, Wine

Goal

To demonstrate the ability of the Thermo Scientific™ iCAP™ 7000 Plus Series ICP-OES to determine trace elements and major components in different red and white wines according to maximum contaminant limits specified by national and international regulations.

Introduction

Oenological laboratories routinely analyze for certain parameters to determine the quality of a wine. Nutritional properties as well as taste, smell and appearance of the wine are influenced by the presence of chemical elements. Certain elements fall under country specific regulation for consumption or export (Table 1).

Table 1. Concentration limits for elements in wine according to specific regulations and organizations (in $\mu g \cdot g^{-1}$).

	Al	As	Boric acid	Cd	Cu	Na	Pb	Sn	Zn
Chilean Decree 78 of 1986	-	0.2	-	0.01	1	-	0.15	-	-
Deutsche Weinverordnung	8	0.1	80	0.01	2	-	0.25	1	5
EU Regulation No 1881/2006	-	-	-	-	-	-	0.2	-	-
Health Canada	-	0.1	-	-	1	-	0.2	25	-
OIV	-	0.2	80	0.01	1	80	0.15	-	5
WHO (CODEX STAN 193-1995)	-	-	-	-	-	-	0.2	-	-

OIV: International Organization of Vine and Wine
WHO: World Health Organization

The natural level of trace elements in wine is typically nontoxic. Agricultural practice however can change the composition of the trace element budget of the vineyard, for example of Hg, Pb, Sn, and Zn. Elements such as Cu, Mn, and Zn are increased due to use of fertilizers and pesticides. In addition, the acidity of wine and must (freshly pressed grape juice) can dissolve Cr, Cu, Ni, and Zn from wine making equipment like pumps and taps. Due to these processes the concentration of heavy metals like As, Cd, Hg and Pb can rise and reach toxic levels. Therefore, the quality of the wine has to be determined not only for nutritional reasons but also for consumer safety.

Table 2. Effect of certain elements on wine.

Element	Effect on wine
Cu, Fe, Mn	Destabilization and oxidative evolution
Al, Cu, Fe, Ni, Zn	Haze formation, changes of taste and smell

Instrumentation

For the sample analysis, the Thermo Scientific iCAP 7400 ICP-OES Duo was used together with an aqueous sample introduction kit, consisting of a concentric glass nebulizer and a cyclonic glass spray chamber as well as a 1.5 mm injector tube. The duo configuration was chosen for its ability to detect trace elements such as toxic heavy metals (As, Cd, Hg, Pb) in axial view and matrix components in radial view. A Teledyne CETAC ASX-560 autosampler was used to transfer the sample to the introduction system of the ICP-OES. The Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software was used for data acquisition and provides easy options for post-analysis data manipulation.

Sample preparation

All calibration and spike solutions were prepared from 1000 µg·g^{-1} single element solutions (SPEX CertiPrep Group, Metuchen, US). The individual solutions were made with 18 MΩ ultra-pure water and trace metal grade HNO$_3$ (67-69%, Fisher Chemical, Loughborough, UK) as well as analysis grade ethanol (99.8+ %, Fisher Chemical, Loughborough, UK), to a final concentration of 0.1 % HNO$_3$ for each solution and 1.2 % ethanol for major components and 12 % ethanol for trace elements. To account for physical interferences due to different matrices in the wine, an internal standard solution of Y (100 µg·g^{-1}) was added to all solutions to make up a final concentration of 1 µg·g^{-1} Y. Three wines from different regions were analyzed, a white (Grüner Veltliner, Austria), a rosé (Portugieser Pinot Noir, Germany) and a red wine (Cabernet Sauvignon, Chile). They were diluted to a ratio of 1:10 for major components and the analysis of trace elements was done directly. The accuracy for all elements analyzed was tested by spiking the samples with a concentration in the middle of the calibration range.

Since boric acid (Table 1) cannot be analyzed as such via ICP-OES, total B is analyzed in its elemental form. Afterwards, a correction factor of 5.7197 is applied to the measured B concentration, assuming that all B in the sample is present in the form of boric acid. In the event that the boric acid level is exceeded, investigation in to the specific B species will have to take place.

Method development and analysis

A method was created in the Qtegra ISDS software. The wavelengths used for analysis are shown in Table 5, these were selected as they were free from interferences and provided the sensitivity to quantify the elements of interest in the expected concentration range. The parameters used for the method can be found in Table 4. The plasma was ignited and the instrument allowed to warm up for a period of 15 minutes. A spectrometer optimization was performed directly before analysis.

Table 4. Method parameters.

Parameter	Setting	
Pump tubing	Sample Tygon® white/white Drain Tygon® blue/yellow	
Pump speed	50 rpm	
Spray chamber	Glass cyclonic	
Nebulizer	Glass concentric	
Nebulizer gas flow	0.55 L·min^{-1}	
Coolant gas flow	12 L·min^{-1}	
Auxiliary gas flow	0.5 L·min^{-1}	
Center tube	1.5 mm	
RF Power	1150 W	
Wash time	30 s	
Exposure time	Axial view	Radial view
	UV 15 s, Vis 5 s	Vis 5 s

Table 3. Concentrations of calibration standards and spiked sample in µg·g^{-1}.

Element/ Standard	Calibration for major components (diluted samples)				Calibration for trace components (undiluted samples)				Spiked sample
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	
Al	0.08	0.2	0.4	0.8					0.40
As					0.0075	0.03	0.12	0.6	0.024
B	0.14	0.35	0.70	1.4					0.71
Ca	1	2.5	5	10					5
Cd					0.00075	0.003	0.012	0.06	0.0024
Co					0.002	0.008	0.032	0.16	0.0064
Cr					0.008	0.032	0.128	0.64	0.026
Cu	0.01	0.025	0.05	0.1					0.050
Fe	0.095	0.2375	0.475	0.95					0.49
K	10	25	50	100					50
Mg	1.5	3.75	7.5	15					7.6
Mn	0.03	0.075	0.15	0.3					0.15
Na	0.8	2	4	8					4.0
Ni	0.0017	0.00425	0.0085	0.017					0.008
Pb					0.0375	0.15	0.6	3	0.12
Sn	0.01	0.025	0.05	0.1					0.05
Zn	0.05	0.125	0.25	0.5					0.25

Following method development, the instrument was calibrated and the samples were analyzed. Accuracy of the method was shown by determination of the correlation coefficient of the calibration and the recovery of a spike in all samples (Table 5).

A method detection limit study was carried out by analyzing the calibration blank with ten replicates and multiplying the standard deviation of this analysis by three. This was repeated three times and the average values for detection limits were calculated (Table 6).

Figure 1. Calibration curve for Pb 220.353 nm.

Results

The linearity of the calibration curves is very good with values greater than 0.998 for each wavelength. An exemplary calibration curve for Pb 220.353 nm is shown in Figure 1. Most of the recoveries of the spiked samples are within a range of 95 - 105 % (Table 5). Only some results are outside this range as for example K, As and Pb.
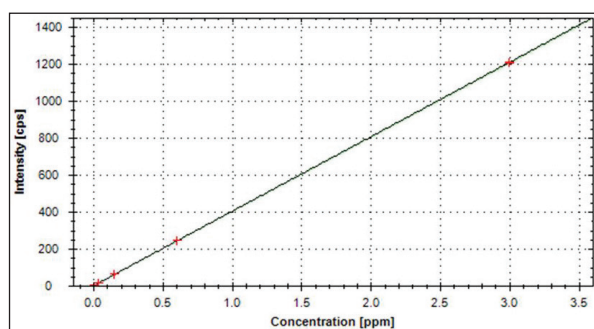
Table 5. Correlation coefficients R², internal standard wavelengths used for corrections of physical interferences and absolute as well as percentage recovery values per wavelength and sample. Concentrations are given in µg·g⁻¹.

Element and wavelength (nm)	View	R²	Internal standard (nm)	White wine spike	Recovery (%)	Rosé wine spike	Recovery (%)	Red wine spike	Recovery (%)
Al 396.152	Radial	0.9990	Y 360.073	0.40	100.0	0.41	102.5	0.40	100.0
As 193.759	Axial	0.9998	Y 224.306	0.024	100.0	0.024	100.0	0.021	87.5
B 249.773	Radial	0.9986	Y 371.030	0.71	100.0	0.730	102.8	0.72	101.4
Ca 315.887	Radial	0.9989	Y 324.228	5.02	100.4	5.26	105.2	5.06	101.2
Cd 226.502	Axial	1.0000	Y 224.306	0.0024	100.0	0.0025	104.2	0.0024	100.0
Co 230.786	Axial	1.0000	Y 224.306	0.0063	98.4	0.0065	101.6	0.0064	100.0
Cr 283.563	Radial	1.0000	Y 324.228	0.026	100.0	0.027	103.8	0.026	100.0
Cu 324.754	Radial	0.9992	Y 324.228	0.050	100.0	0.051	102.0	0.050	100.0
Fe 259.940	Radial	0.9989	Y 324.228	0.48	98.0	0.49	100.0	0.49	100.0
K 769.896	Radial	0.9996	Y 360.073	47	94.0	50	100.0	45	90.0
Mg 280.270	Radial	0.9993	Y 324.228	7.4	97.4	7.6	100.0	7.4	97.4
Mn 257.610	Radial	0.9989	Y 377.433	0.145	96.7	0.150	100.0	0.151	100.7
Na 588.995	Radial	0.9996	Y 360.073	4.0	100.0	4.1	102.5	4.0	100.0
Ni 231.604	Axial	0.9988	Y 371.030	0.008	100.0	0.008	100.0	0.008	100.0
Pb 220.353	Axial	0.9999	Y 377.433	0.113	94.2	0.113	94.2	0.115	95.8
Sn 283.999	Axial	0.9994	Y 324.228	0.05	100.0	0.05	100.0	0.05	100.0
Zn 213.856	Radial	0.9993	Y 324.228	0.245	98.0	0.251	100.4	0.250	100.0

K shows lower recoveries in the white (94%) and red wine (90%). The concentration of K in these wines is very high. Even in the diluted samples K shows concentrations of approximately 70 and 120 µg·g⁻¹, which leads to spiked concentrations being above the calibration curve (120 and 170 µg·g⁻¹). These results fall into the range where self-absorption of K occurs and therefore the signal is non-linear.

The worse recovery of As may be explained by the fact that the spike concentration is just at the quantification limit (quantification limit = 3 times the detection limit).

Table 6. Analyte concentrations for the three wine samples, method detection limits and limit values. Concentrations are given in µg·g⁻¹.

Element and wavelength (nm)	White wine	Rosé wine	Red wine	Detection limit	Limit value
Al 396.152	3.12	2.23	0.50	0.010	8
As 193.759	<DL	<DL	<DL	0.008	0.1
B 249.773	2.92	2.96	6.30	0.003	-
Boric acid*	16.67	16.93	36.02	-	80
Ca 315.887	78.64	97.69	72.47	0.007	-
Cd 226.502	<DL	<DL	<DL	0.0004	0.01
Co 230.786	0.0067	0.0034	0.0018	0.0001	-
Cr 283.563	0.007	0.032	0.014	0.001	-
Cu 324.754	<DL	0.17	<DL	0.002	-
Fe 259.940	1.43	1.42	3.72	0.002	-
K 769.896	719	492	1178	0.094	-
Mg 280.270	89.73	76.20	109.75	0.0001	-
Mn 257.610	0.80	0.96	1.62	0.0003	-
Na 588.995	29.18	34.43	13.95	0.016	80
Ni 231.604	<DL	<DL	<DL	0.001	-
Pb 220.353	0.028	0.048	0.042	0.008	0.15
Sn 283.999	<DL	<DL	<DL	0.010	1
Zn 213.856	0.42	1.41	0.82	0.001	5

<DL: below detection limit
*Calculated as B·5.7197

Detection limits in the wine matrix are at least 10 times below the limit value (lowest contaminant level, see Table 1) for each analyte. This means, that the necessary analytes can be quantified correctly in the wine matrix. All wines tested show values that are in accordance with the limit values.

Conclusion

Careful selection of the internal standard wavelengths is crucial for analyses in this complex matrix. Further dilution (higher than 1:10) may be necessary for some elements.

The UV region suffers from strong CO interferences and background points are difficult to be set. This is especially true for trace elements like As, Cd, Co, Ni, and Pb. Enlarging the peak observation area may help to find more appropriate background points. Due to the good detection limits a further dilution could also be done for trace components without compromising the ability to quantify correctly below the limit values.

The analysis shows that the Thermo Scientific iCAP 7000 Plus Series ICP-OES delivers excellent accuracy and sensitivity for determination of nutrients and trace elements in wines in conformity with the present recommendations for concentration limits. Moreover, very good spike recoveries indicate that an internal standard is capable of correcting for physical interferences induced by this complex sample matrix. In addition to the robust instrument performance, the powerful software platform Qtegra ISDS simplifies method development and makes post-processing of the sample data an easy operation.

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