APPLICATION NOTE

Analysis of Trace Elements in Whisky Using the Thermo Scientific iCAP 7000 Plus Series ICP-OES

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Key Words
Beverages, Spirits, Trace Elements, Whisky, Whiskey

Goal

This application note demonstrates the ability of the Thermo Scientific iCAP 7000 Plus Series ICP-OES to determine trace elements and major components in whisky. The method can be applied to drinks with similar alcohol content.

Introduction

The production of whisky is a complex multiple step process. One of the key stages is distillation which may occur more than once; copper plays an important part in this distillation process as the vessels used for the distillation are typically copper. Copper is used as it has beneficial properties including good heat conduction, and catalytic properties. It has the ability to neutralize sulfur compounds, which are considered to possess unpleasant and undesirable aromas which negatively affect the final product. However, contamination of arsenic in the final product leach from copper equipment during the whisky manufacture could reach toxic concentrations if poor quality copper equipment is used. Other metal or trace element contaminants can come from raw ingredients used for the production. Elements such as manganese, zinc, lead or cadmium can be introduced from the water or grain used in production and the likely hood of their presence is increased due to use of fertilizers and pesticides.

Therefore the measurement of trace elements in alcoholic beverages is required to comply with regulations and to ensure the quality of the final products, for consumer safety. The analysis of contaminants in beverages in Europe is based on the recommendation of the European Union “Reports on tasks for Scientific Cooperation” (SCOOP, Task 3.2.11) and the Committee on Toxicity (COT; Chemicals in Food, Consumer Products and the Environment) which researched and established the average human intake and absorption of contaminants and nutrients from liquids.

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Instrumentation

For this analysis the Thermo Scientific™ iCAP™ 7600 ICP-OES Duo was used with the organics sample introduction kit, consisting of the components listed in Table 2. The duo system configuration was chosen because of its ability to detect trace elements such as toxic heavy metals (arsenic, cadmium, lead) and major nutrient components. 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.

Figure 1. Thermo Scientific iCAP 7000 Plus Series ICP-OES.

Sample preparation

Calibration standards and spike solutions were prepared from single element solutions (1000 $mg \cdot l^{-1}$, SPEX CertiPrep Group, Metuchen, US). The individual solutions were made with 18 MΩ ultra-pure water and trace metal grade nitric acid (67-69%, Fisher Chemical, Loughborough, UK) as well as analysis grade ethanol (99.8+%, Fisher Chemical, Loughborough, UK), to a final concentration of 0.2% nitric acid for each solution and 40% ethanol. To account for physical interferences due to different matrices in the whisky, an internal standard solution of yttrium (10 $mg \cdot l^{-1}$) was added to all solutions online via a T-piece. Five different whiskies were analyzed, a Welsh single malt (Penderyn 46%), a Indian single malt (Amrut Peated Indian single Malt Whisky 46%) and three different Irish whiskeys (Jameson, Bushmills and Kilbeggan 40%). The accuracy for trace elements analyzed was tested by spiking the samples with a concentration of 100 $\mu g \cdot l^{-1}$ of the elements used for the Calibration.

Table 1. Calibration standard concentrations ($\mu g \cdot l^{-1}$).

Element and Wavelength (nm)	View	Blank	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7	STD 8	STD 9
Na 589.592	Axial	0	0	0	0	0	0	250	750	2500	7500
K 766.490	Axial	0	0	0	0	0	0	250	750	2500	7500
Ca 393.366	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Cr 283.563	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Mn 257.610	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Fe 238.204	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Co 238.892	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Ni 231.604	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Cu 324.754	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Zn 213.856	Radial	0	0.5	2.5	7.5	25	75	250	750	0	0
As 189.042	Radial	0	0.5	2.5	7.5	25	75	250	750	0	0
Cd 214.438	Radial	0	0.5	2.5	7.5	25	75	250	750	0	0
Ba 455.403	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0
Pb 220.353	Radial	0	0.5	2.5	7.5	25	75	250	750	0	0
Mg 279.553	Axial	0	0.5	2.5	7.5	25	75	250	750	0	0

Method development and analysis

A LabBook was created using the Qtegra ISDS Software. For each element, wavelengths were selected using the intuitive wavelength selection tool of the Qtegra ISDS Software. The wavelengths used for analysis are shown in Table 1, 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 2. The plasma was ignited and the instrument allowed to warm up for a period of 20 minutes.

A torch alignment and a spectrometer optimization was performed directly before analysis and a detection limit study was carried out by analyzing the calibration blank three times with ten replicates and multiplying the standard deviation of this analysis by three. To ensure freedom from interferences, the subarray plots were examined and background correction points were set appropriately.

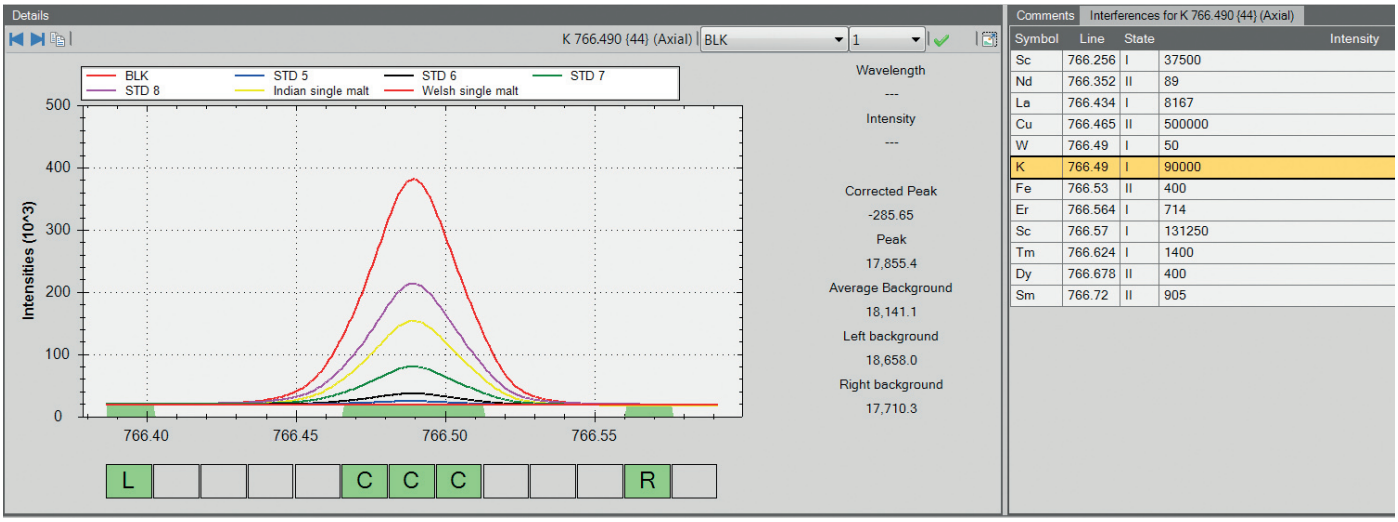

Figure 2. Subarray plot for K 766.490 nm, indicating the peak center and background points.

Table 2. Instrument parameters.

Parameter	Setting	
Pump Tubing	Sample solvent flex white/white	
	Drain solvent flex orange/blue	
	Internal Standard Tygon™ orange/green	
Pump Speed	25 rpm	
Spray Chamber	Baffled cyclonic	
Nebulizer	V-groove	
Nebulizer Gas Flow	0.35 L min^{-1}	
Auxiliary Gas Flow	1.5 L min^{-1}	
Coolant Gas Flow	16 L min^{-1}	
Center Tube	1.5 mm	
RF Power	1300 W	
Exposure Time	Axial View	Radial View
	UV 15 s, Vis 15 s	UV 15 s, Vis 15 s

Results

The results obtained for the analysis of the different whisky samples are shown in Table 3 and are further highlighted in Figure 3. Each sample was spiked with the same 1000 $mg \cdot l^{-1}$ solutions used to make the calibration standards. These spiked samples were analyzed in the same run as the samples and all recoveries for the trace elements were within the acceptable range of +/-20%.

No spike recovery was performed for sodium, potassium because the concentration of these elements is very high in the whisky samples, which leads to spiked concentrations being above the calibration curve. These results fall into the range where self-absorption occurs and therefore the signal is non-linear. The detection limit study, which is also shown in Table 3, reports values in the single digit $\mu g \cdot l^{-1}$ range or lower. Exceptions are arsenic with 30 $\mu g \cdot l^{-1}$ and lead with 33 $\mu g \cdot l^{-1}$.

All of the trace contaminants detrimental to human health (arsenic, cadmium and lead) were measured and found to be below the regulation limits (Table 4).

Table 3. Results of the analysis Concentrations, Spike recoveries and method detection limits (MDL) are given in $\mu g \cdot l^{-1}$.

Element	Indian single malt	Spike recovery (%)	Welsh Single malt	Spike recovery (%)	Irish Jameson	Spike recovery (%)	Irish Bushmills	Spike recovery (%)	Irish Kilbeggan	Spike recovery (%)	MDL (µg/L)
Na	769	N/A	2160	N/A	7182	N/A	4890	N/A	7901	N/A	1.17
K	5271	N/A	13976	N/A	4795	N/A	5246	N/A	2101	N/A	1.74
Ca	250	102	501	95	307	101	217	106	428	108	0.06
Cr	<DL	102	<DL	102	8.69	104	<DL	107	<DL	108	1.30
Mn	19.8	103	23.9	103	7.45	105	6.11	107	4.82	109	0.30
Fe	41.7	101	21.8	101	28.1	103	24.8	104	21.7	108	2.19
Co	<DL	103	<DL	104	<DL	106	<DL	107	<DL	108	3.09
Ni	4.78	102	6.48	102	0.0296	106	<DL	107	<DL	108	3.67
Cu	1636	86	131	108	21.5	106	46.1	110	37.2	112	1.34
Zn	33.4	108	21.7	101	3.06	105	2.33	106	4.50	108	1.47
As	41.8	89	39.8	81	<DL	101	<DL	114	<DL	114	30.1
Cd	2.03	103	<DL	105	<DL	106	<DL	107	<DL	109	1.94
Ba	0.764	106	4.36	105	1.33	105	0.794	106	0.493	109	0.12
Pb	<DL	100	<DL	85	<DL	87	<DL	95	<DL	100	33.4
Mg	318	100	473	97	99.7	104	69.1	106	73.8	107	0.06

<DL: below detection limit.

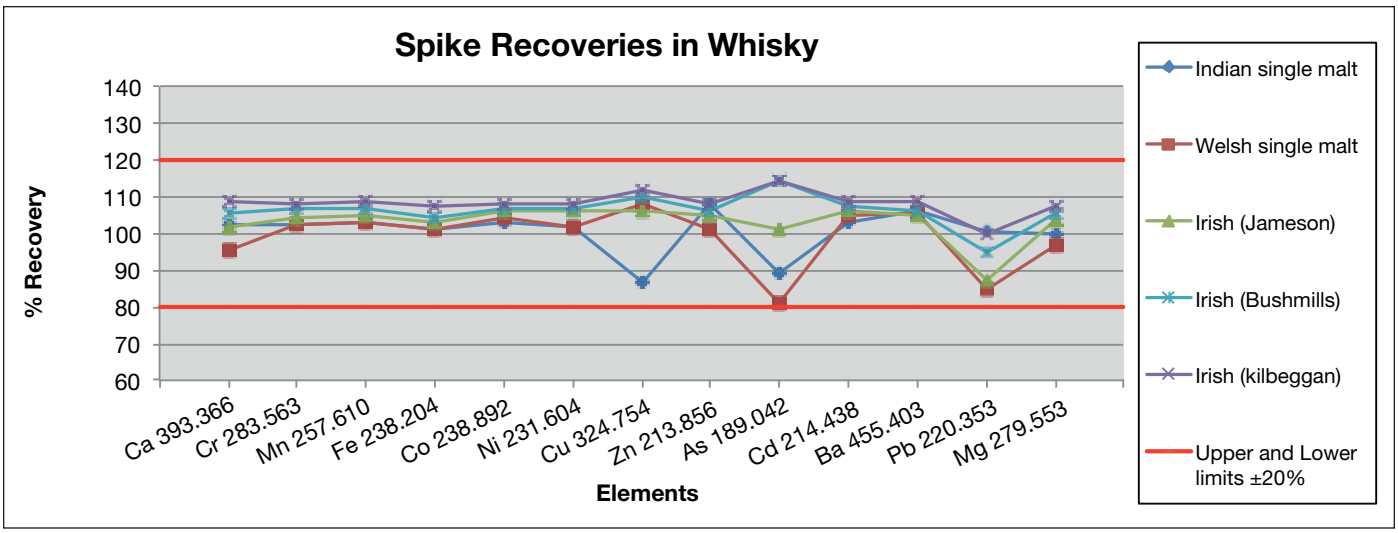

Figure 3. Results obtained for the analysis of the different Whisky samples.

Table 4. Typical regulation maximum allowed concentrations in various beverages.

Element	Maximum concentration (mg/L)
As	<0.2
Cd	<0.1
Cu	<2
Fe	<7
Pb	<0.5

Conclusion

Usually, radial instruments are used for the analysis of organic samples because of their higher matrix tolerance and reduced interferences. However, this study demonstrates that also the iCAP 7600 ICP-OES Duo delivers robust performance when analyzing the complex sample matrix of whisky. Although a viewing height for the radial measurement cannot be selected, careful selection of interference-free wavelengths allows you to determine very low detection limits (single $\mu g \cdot l^{-1}$) and excellent accuracy, proving that the iCAP 7600 ICP-OES Duo is an ideal choice for analysis of trace elements in alcoholic beverages.

The UV region suffers from strong carbon-oxygen interferences and background points are difficult to be set. This is especially true for trace elements like arsenic, cadmium, cobalt, nickel, and lead. Enlarging the peak observation area may help to find more appropriate background points. In addition to the robust instrument performance, the powerful software platform Qtegra ISDS Software simplifies method development and makes post-processing of the sample data an easy operation.

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