Elemental profiles of whiskies allow differentiation by type and region by inductively coupled plasma – optical emission spectroscopy (ICP-OES)

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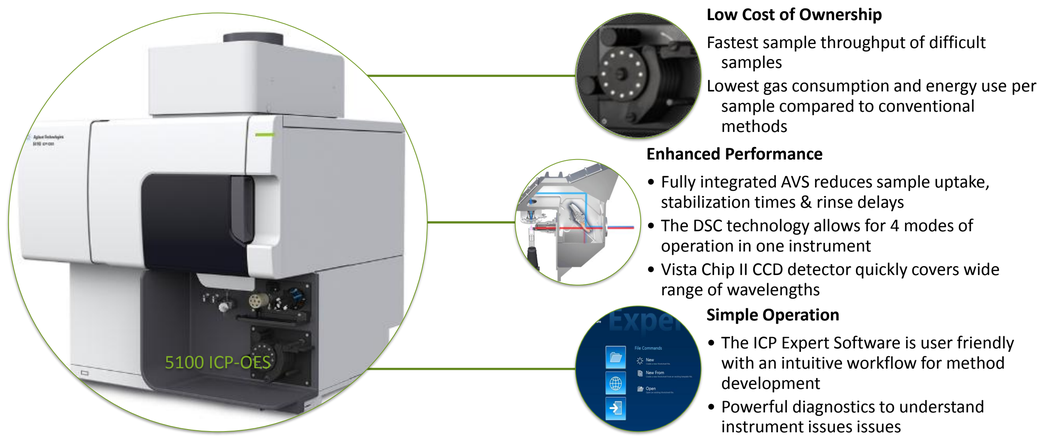
Introduction

The analysis of the elemental composition of whiskies provides important information whether being used to determine the sample origin or understanding how different whiskey styles are caused by processing equipment and raw materials. Therefore, profiling whiskies for trace elements could be a way to define different styles based on their micro-elemental composition. The purpose of this study was to differentiate various whiskey styles by evaluating the elemental composition of Whiskey samples

Sixty-nine commercial whiskies were selected for this study, including: 33 single malt scotch, 16 Bourbon, 8 Irish, 2 Tennessee, 1 American Rye, and 9 Japanese whiskies. The whiskies varied in age from seven to twenty-seven years, and were analyzed on an Agilent 5100 ICP-OES system by direct dilution. Twenty-eight elements were quantified using matrix-matched calibration standards and the final data analyzed with the Agilent Mass Profiler Professional.

Instrumental



Experimental

Samples

- 69 whiskey samples (Table 1)
- Whiskies: 16 Bourbon (B), 8 Irish (I), 9 Japanese (J), 1 Rye (R), 33 Scotch (S), 2 Tennessee (T)
- Products from the same distillery are indicate
- The regions of the scotch whiskies are indicated: Island (A), Islay (B), Lowland (C), Highland (D), Speyside (E), Campbeltown (F)

Experimental Setup

- Samples were diluted 1:20 in 1% HNO_3 and 0.5% HCl (v/v).
- Calibration standards, QCs, and CRMs were matrix matched and diluted with 1% HNO_3 and 0.5% HCl and 4% ethanol
- Instrument conditions and samples in Figure 2a and 2b.

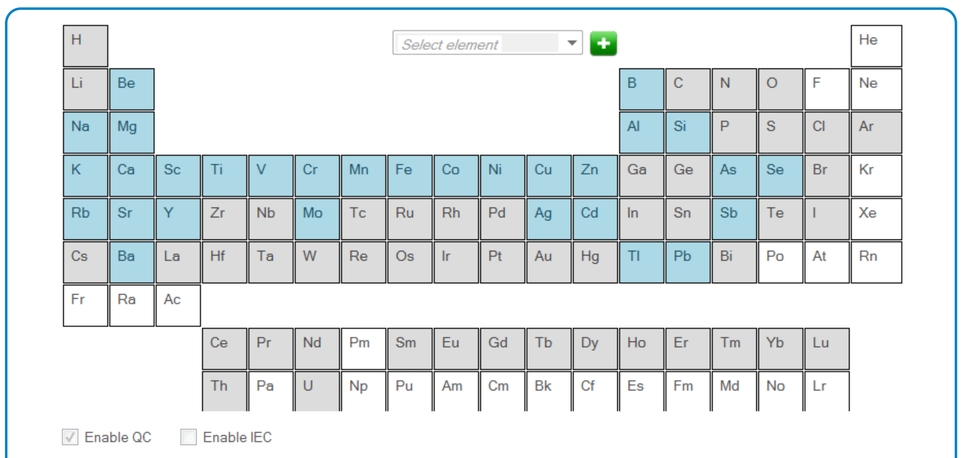


Figure 1: The elements that were analyzed in the whiskey samples are marked in blue.

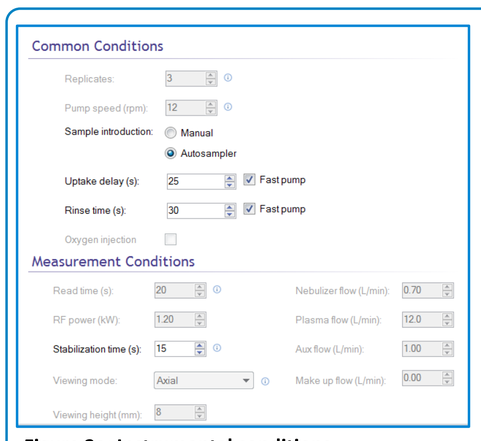


Figure 2a: Instrumental conditions.

Figure 2b: The Whiskey samples.

The Whiskey samples were analyzed using the Agilent 5100 ICP-OES by direct dilution. The elements that were measured are shown in Figure 1. To ensure the accuracy of the given method, QCs and CRMs were analyzed every ten samples.

Table 1: Whiskey sample codes, age (if known; N.A. if unknown) and proof are given for each sample. Whisk(e)y types include: Bourbon (B), Irish (I), Japanese (J), Scotch (S), Tennessee (T). Regions for Scotch whiskies and samples from the same distillery are indicated in brackets after the distillery code. Regions include: Island (A), Islay (B), Lowland (C), Highland (D), Speyside (E), Campbeltown (F).

Code	Age	Proof	Distillery	Code	Age	Proof	Distillery	Code	Age	Proof	Distillery
B1	7	107	D1	I7	15	92	D13	S13	12	80	D25 (E)
B2	8	80	D1	I8	12	92	D13	S14	10	80	D26 (E)
B3	N.A.	90	D2	J1	12	86	D14	S15	15	92	D26 (E)
B4	N.A.	100	D2	J2	12	86	D14	S16	21	86	D26 (E)
B5	10	90	D2	J3	N.A.	96	D15	S17	12	80	D27 (E)
B6	N.A.	86.6	D2	J4	N.A.	110	D15	S18	15	80	D27 (E)
B7	N.A.	100	D3	J5	10	90	D16	S19	12	86	D28 (C)
B8	12	86	D1	J6	12	90	D16	S20	12	86	D29 (D)
B9	N.A.	101	D4	J7	N.A.	80	D16	S21	10	80	D30 (D)
B10	N.A.	90	D5	J8	17	86	D16	S22	12	80	D31 (A)
B11	9	100	D1	J9	12	80	D16	S23	18	86	D31 (A)
B12	N.A.	114	D4	S1	10	86	D17 (A)	S24	10	80	D32 (A)
B13	N.A.	90.2	D6	S2	10	92	D18 (B)	S25	16	80	D32 (A)
B14	N.A.	90.4	D7	S3	12	80	D19 (C)	S26	16	86	D33 (B)
B15	12	90	D2	S4	18	86	D19 (C)	S27	10	80	D34 (B)
B16	N.A.	113	D8	S5	27	116	D19 (C)	S28	15	86	D34 (B)
R1	12	80	D16	S6	12	92.6	D20 (B)	S29	12	80	D35 (E)
I1	N.A.	80	D9	S7	12	86	D21 (B)	S30	12	80	D36 (D)
I2	N.A.	80	D10	S8		88	D22 (D)	S31	16	80	D37 (A)
I3	N.A.	80	D11	S9	10	80	D23 (D)	S32	15	92	D38 (F)
I4	8	80	D12	S10	10	80	D23 (D)	S33	10	86	D30 (D)
I5	N.A.	80	D12	S11	12	80	D24(E)	T1	N.A.	90	D39
I6	12	115	D13	S12	15	92	D24 (E)	T2	N.A.	80	D40

Results and Discussion

The 5100 ICP-OES sports a wide analytical range which allows for excellent linearity at high concentrations, as seen in the example calibration curves in Figure 2. The excellent instrument performance is demonstrated by the limit of detection (LOD) for each element and the wide analytical range (Table 2).

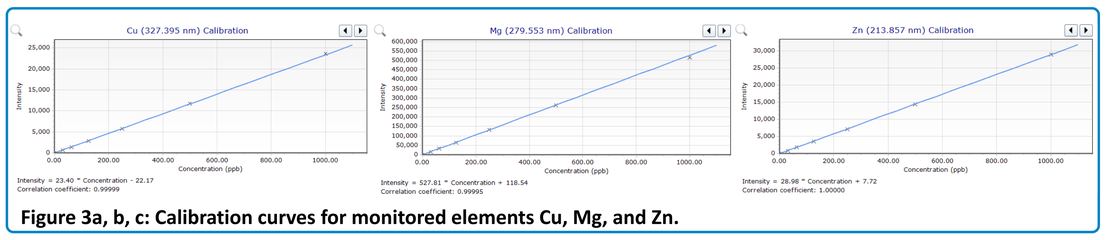


Figure 3a, b, c: Calibration curves for monitored elements Cu, Mg, and Zn.

Table 2: The LOD and concentration range for each analyzed element.

Element		LOD [µg/L]	Min-Max [µg/L]	Element		LOD [µg/L]	Min-Max [µg/L]
Ag	328.068 nm	0.167	0.00E+00 - 0.00E+00	Mn	257.610 nm	0.039	7.40E-01 - 2.03E+02
As	193.696 nm	5.373	0.00E+00 - 0.00E+00	Na	588.995 nm	2.286	4.40E+02 - 2.56E+04
B	249.772 nm	0.230	1.76E+01 - 5.02E+02	Ni	231.604 nm	2.015	0.00E+00 - 0.00E+00
Ba	455.403 nm	0.112	1.13E+00 - 1.59E+02	Pb	220.353 nm	1.963	0.00E+00 - 0.00E+00
Be	313.042 nm	0.043	0.00E+00 - 0.00E+00	Rb	421.552 nm	0.032	1.45E+00 - 5.76E+01
Ca	396.847 nm	0.029	2.47E+02 - 9.29E+03	Se	196.026 nm	8.861	0.00E+00 - 0.00E+00
Cd	214.439 nm	0.137	1.95E+01 - 1.95E+01	Si	251.611 nm	2.085	1.89E+02 - 1.93E+04
Co	238.892 nm	0.994	0.00E+00 - 0.00E+00	Sr	407.771 nm	0.017	1.85E+00 - 5.70E+01
Cr	267.716 nm	0.262	3.63E+00 - 4.92E+01	Ti	336.122 nm	1.305	0.00E+00 - 0.00E+00
Cu	327.395 nm	0.229	2.06E+01 - 2.45E+03	Tl	190.794 nm	3.493	0.00E+00 - 0.00E+00
Fe	238.204 nm	0.203	3.61E+00 - 7.54E+02	V	292.401 nm	0.455	0.00E+00 - 0.00E+00
K	766.491 nm	4.024	3.52E+03 - 4.72E+04	Zn	213.857 nm	0.219	6.94E+00 - 8.20E+02
Mg	279.553 nm	0.020	1.26E+01 - 5.02E+03				

Results and Discussion

The exceptional performance of the 5100 ICP-OES while analyzing the Whiskey samples was also shown in the spike recovery data. Samples were spiked to a final concentration of 5 µg/kg with each of the elements listed in Table 3. The results showed all recoveries were within ± 10% with the exception of K and Na (Table 3).

Table 3: The mean percent recoveries ± 1σ and the recovery range from the spike analysis.

	Al	As	B	Ba	Be	Ca	Cd	Co	Cr
Wavelength (nm)	396.152	193.696	249.772	455.403	313.042	396.847	226.502	238.892	267.716
Mean Recovery ± 1σ	101 ± 1%	108 ± 2%	99 ± 2%	100 ± 1%	108 ± 1%	97 ± 5%	99 ± 1%	98 ± 1%	98 ± 1%
Recovery Range	100-103%	106-109%	98-101%	99-102%	107-110%	93-102%	98-100%	97-99%	97-100%
	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb
Wavelength (nm)	327.395	238.204	766.491	279.553	257.610	202.032	588.995	231.604	220.353
Mean Recovery ± 1σ	100 ± 2%	99 ± 1%	70 ± 110%	98 ± 6%	105 ± 0%	100 ± 2%	88 ± 31%	99 ± 1%	98 ± 2%
Recovery Range	99-103%	97-100%	-49-167%	91-104%	105-105%	98-101%	54-112%	98-100%	96-100%
	Rb	Se	Si	Sr	Ti	Tl	V	Zn	
Wavelength (nm)	421.552	196.026	251.611	407.771	336.122	190.794	292.401	213.857	
Mean Recovery ± 1σ	101 ± 1%	105 ± 0%	95 ± 5%	100 ± 1%	100 ± 1%	92 ± 9%	101 ± 1%	98 ± 1%	
Recovery Range	100-102%	105-105%	90-101%	99-101%	99-101%	82-101%	100-102%	97-99%	

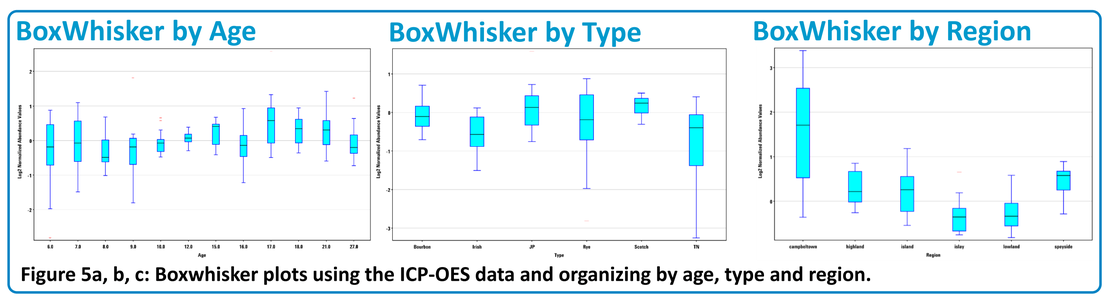


Figure 5a, b, c: Boxwhisker plots using the ICP-OES data and organizing by age, type and region.

The exploratory data analysis was completed using Agilent's Mass Profiler Professional (MPP). The resultant BoxWhisker plots are given in Figures 5. Slight differences in each plot can be noted. This suggests that the element profiles of whiskies could be used to distinguish samples based on the age, type, and region of the sample. It is possible if more elements are analyzed in the future, greater separation between samples could occur. The PCA bi-plot in Figure 6 confirms this assumption as it can be seen some of the whiskey types, such as the Irish samples, are separated from the others. This separation is correlated to elements Na, Ba, and Zn.

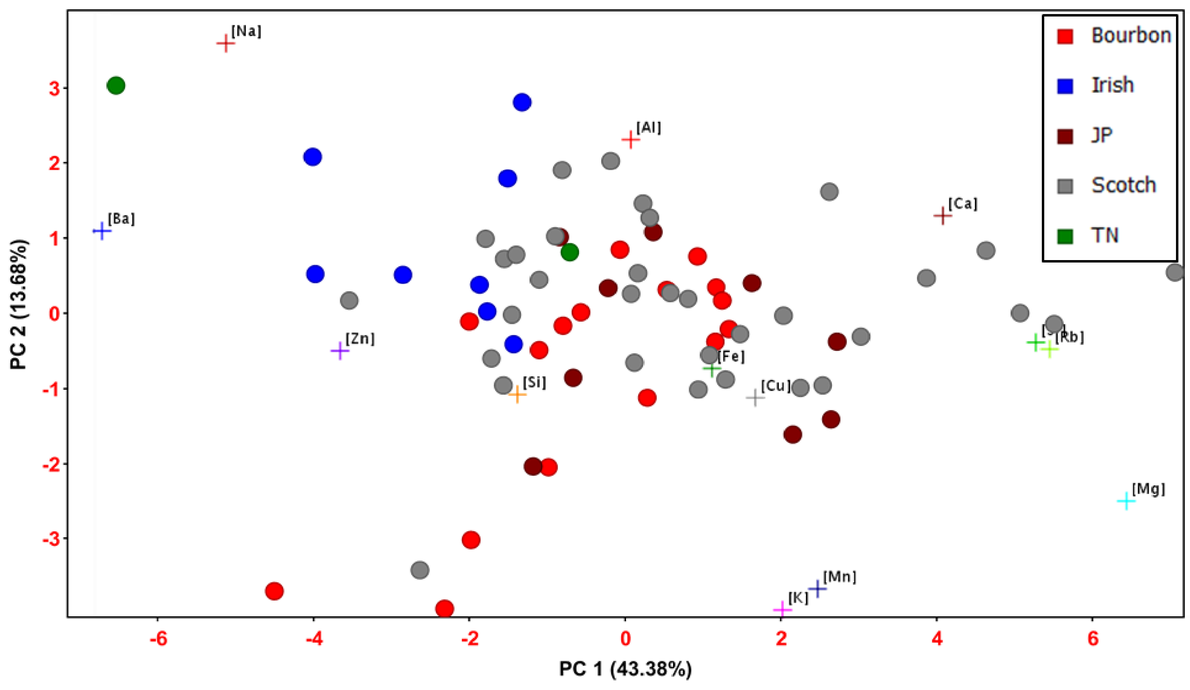


Figure 6. A Principal Component Analysis (PCA) plot showing the separation of different whiskies by their elemental composition. The PCA score plot and PCA loading plot are overlaid to show the contribution of each element to the separation of the samples along PC 1 (43.38%) and PC 2 (13.86%). Each of the 5 Whiskey types (non-averaged) are color-coded: Green-Tennessee; Blue- Irish; Red-Bourbon; Gray -Scotch; Brown-Japanese.

Conclusions

The Agilent 5100/5110 ICP-OES is a viable tool for elemental profiling of various types of whiskies. The instrumental design allowed for fast and easy analysis of the samples with low detection limits for each measured element. Analysis of the spikes showed the method was precise and accurate. The preliminary data analysis of the whiskies showed that element compositions could possibly be used to differentiate samples based on age, type, and region. Further research is needed, with collaboration from the industry, to fully understand the degree element profiles can be used in whiskey research.