Application note | 002971

Food and beverage

Profiling the elemental composition of whisky using inductively coupled plasma mass spectrometry (ICP-MS)

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Keywords

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Goal

This application note will highlight how whisky samples can be comprehensively analyzed for their elemental composition and how this can help to unravel differences according to their geological origin as well as in the processing.

Introduction

The fermentation of foods and grains has a long history in human civilizations. Fermentation (and subsequent production of alcoholic beverages) has helped to make foods and drinks more durable, for example as an alternative to quickly degrading drinking water supplies on sea travel.

Whisky refers to a liquor made from fermented grain mash, often barley, corn, rye, and wheat. The main whisky producing countries are Scotland, Ireland, and the US, and controls over geographic origin are in place to maintain overall brand integrity.

Due to the large profit range especially for aged and rare whisky from specific manufacturers or regions, adulteration or incorrect labeling causes issues. There are a series of marker compounds that can be analyzed using gas chromatography-mass spectrometry to identify whisky adulteration,[1] but the elemental composition can also provide relevant insights. There are certain elements that are known to vary in soils and may be used as indicators for geographical origin or to characterize relevant and unique steps in manufacturing. However, due to the distillation process, they may be depleted significantly in the final spirit compared to the original grain. This means highly sensitive instrumentation is needed to detect potentially small differences in concentrations.

Due to the alcohol content of around 40%, direct analysis using ICP-MS is often not possible. However, a reduction of the alcohol content by dilution makes the analysis possible without major changes to the sample introduction system (i.e., addition of oxygen to the plasma). Spectral and physical interferences however need to be considered. First, the remaining alcohol content changes the viscosity of the sample solutions and will therefore affect flow rates and nebulization efficiency in the sample introduction system. This can be addressed by preparation of matrix-matched calibration standards. Another reason to use matrix-matched calibration standards is the fact that analytes like arsenic and selenium are prone to signal enhancement in the presence of carbon and may therefore lead to false positive results if this is not compensated for. Last but not least, carbon can contribute to the formation of polyatomic interferences, such as $^{40}Ar^{12}C^+$ on ^{52}Cr.

Experimental

A Thermo Scientific™ iCAP™ MSX ICP-MS with a Thermo Scientific™ iSC-65 Autosampler was used for analysis. The instrument was operated using the configuration and parameters highlighted in Table 1. To ensure the best possible sensitivity for detection and quantification of analytes present at ultra-trace levels only (i.e., lanthanide elements), the instrument was operated in the Sensitivity Mode, leveraging a series of key features of the new Thermo Scientific™ iCAP™ MX Series ICP-MS. The Sensitivity Mode optimizes the vacuum in the interface region and leverages the Intellilens feature, that applies dynamically adjusted lens voltages for every analyte to ensure optimum transmission through the mass spectrometer.

To remove polyatomic interferences, kinetic energy discrimination (KED) using pure helium was the measurement mode for all analytes. For all unknown samples, a full mass spectrum was acquired using the Survey Scan option in Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution software. This feature is helpful when analyzing unknown samples as it allows screening for potentially unexpected interferences and confirmation of the presence or absence of analytes initially not included in the analysis, as well as an estimation of their concentration under certain conditions.

Table 1. Instrument parameters used on the iCAP MSX ICP-MS

Parameter	Value
Nebulizer	iCAP MX Series nebulizer
Interface cones	Pt-tipped sample and skimmer
Spray chamber	Cyclonic quartz
Injector	Quartz, 1.0 mm ID
Torch	PLUS torch
Auxiliary flow ($L{\cdot}min^{-1}$)	0.8
Cool gas flow ($L{\cdot}min^{-1}$)	14
Nebulizer flow ($L{\cdot}min^{-1}$)	0.63
CRC conditions	4.9 $mL{\cdot}min^{-1}$ He, 3 V energy barrier
RF power (W)	1,550
Sampling depth (mm)	5
Number of replicates	3
Spray chamber temp. (°C)	2.7
Dwell time	0.1 s per isotope, 0.2 s for ^{75}As, ^{78}Se, and ^{111}Cd
Sweeps	10

Sample and standard preparation

A total of 10 samples from different origins were analyzed as part of the study.

Five out of the ten samples were Scottish whiskies, four samples were of unknown origin, and one was a French brandy sample. The samples were received in glass bottles, but unfortunately no empty bottles were available to test for potential leaching of contaminants into the samples. All samples were diluted volumetrically by a factor of four using 1% (v/v) nitric acid in de-ionized water as diluent, and an internal standard solution was added manually (5 $\mu g{\cdot}L^{-1}$ of Rh and Ir final concentration). The internal standard solution was also added to all blanks, calibration standards, and QC checks at the same concentration level. Additionally, four samples were spiked with specific concentrations of the analytes under study to verify the accuracy of the method. As mentioned previously, calibration standards were prepared using aqueous stock solutions followed by their gravimetric dilutions using 10% ethanol in 1% nitric acid.

Results and discussion

Table 2 summarizes all analytes including internal standards, their calibration range, obtained correlation coefficients, and limits of detection. Whereas the instrumental detection limit (IDL) only considers what can be detected by the instrument, the method detection limit also accounts for the dilution performed in preparation of the sample. In some cases, the addition of ethanol to matrix-match the calibration standard has led to an increased background from contaminations present, which leads to a slightly elevated detection limit. For some elements, the increase in background meant that no quantitative assessment could be performed, i.e., aluminum and zinc.

To ensure the ongoing validity of the calibration curve, a QC standard was regularly analyzed as part of the sequence. The standard was prepared independently from the calibration standards but contained similar concentrations as used for the assessment of the linearity, namely 0.05 µg·L^{-1} for rare earth elements (Y, La-Yb, Th) and 0.75 µg·L^{-1} for all other elements.

Figure 1 contains an overview of the average recovery for both QC checks across all replicates (N=7). As can be seen, the QC checks revealed consistent recovery across all elements in the range between 80% and 120%.

The results of the analysis are summarized in Table 3. The amounts detected in the different samples varied from concentrations of less than 10 ng·L^{-1} (detected for some of the lanthanide series elements) up to several µg·L^{-1} for major elements such as sodium or potassium. Although some of the elements were detected at concentrations outside the calibrated range, the results were still considered sufficiently accurate as the intention of this study was primarily to obtain a better understanding of elements that differ among the various samples analyzed. Due to the highly linear response typically observed in ICP-MS, accurate calculated concentrations are usually obtained even if a sample exceeds the calibrated range significantly. For a more detailed characterization, calibration using adjusted concentration ranges could be performed.

Table 2. Analytes' calibration ranges, correlation coefficients (R^2), and detection limits obtained in this study

Analyte	Calibration range [µg·L^{-1}]	R^2	IDL [µg·L^{-1}]	MDL [µg·L^{-1}]
^{7}Li	0.1–50	0.9999	0.035	0.14
^{9}Be		>0.9999	0.003	0.012
^{23}Na	0.1–500	0.998	2.4	9.6
^{24}Mg		0.999	0.70	2.8
^{39}K		0.999	0.92	3.7
^{44}Ca	125–500	0.999	1.4	5.6
^{51}V	0.1–50	0.9999	0.002	0.008
^{52}Cr		>0.9999	0.011	0.044
^{55}Mn		0.9999	0.017	0.068
^{57}Fe		0.9999	0.044	0.176
^{59}Co		0.9999	0.001	0.004
^{60}Ni		0.9999	0.005	0.02
^{63}Cu		0.9999	0.013	0.052
^{71}Ga		0.9999	0.002	0.008
^{75}As		0.9999	0.001	0.004
^{78}Se		0.9999	0.005	0.02
^{85}Rb		0.9999	0.0001	0.0004
^{88}Sr		0.9995	0.0007	>0.001
^{89}Y	0.01–1	0.9995	0.025	
^{103}Rh	Used as an internal standard			
^{107}Ag	0.1–50	>0.9999	0.002	0.008
^{111}Cd		0.9999	0.009	0.036
^{115}In		0.9999	0.006	0.024
^{133}Cs		0.9999	0.0002	>0.001
^{137}Ba		0.9999	0.002	0.008
^{139}La	0.01–1	0.9999	0.00002	>0.001
^{140}Ce		0.9999	0.00013	>0.001
^{141}Pr		0.9999	0.00003	>0.001
^{146}Nd		0.9999	0.00007	>0.001
^{147}Sm		0.9999	0.00004	>0.001
^{159}Tb		0.9999	0.00004	>0.001
^{163}Dy		0.9999	0.00002	>0.001
^{165}Ho		0.9999	0.00001	>0.001
^{166}Er		0.9999	0.00005	>0.001
^{169}Tm		0.9999	0.00002	>0.001
^{172}Yb		0.9999	0.00009	>0.001
^{175}Lu		0.9999	0.00001	>0.001
^{193}Ir	Used as an internal standard			
^{205}Tl	0.1–50	0.9998	0.00002	>0.001
^{208}Pb		0.9995	0.006	0.024
^{209}Bi		0.9999	0.0009	>0.001
^{232}Th		0.9999	0.0003	>0.001
^{238}U		0.9999	0.00003	>0.001

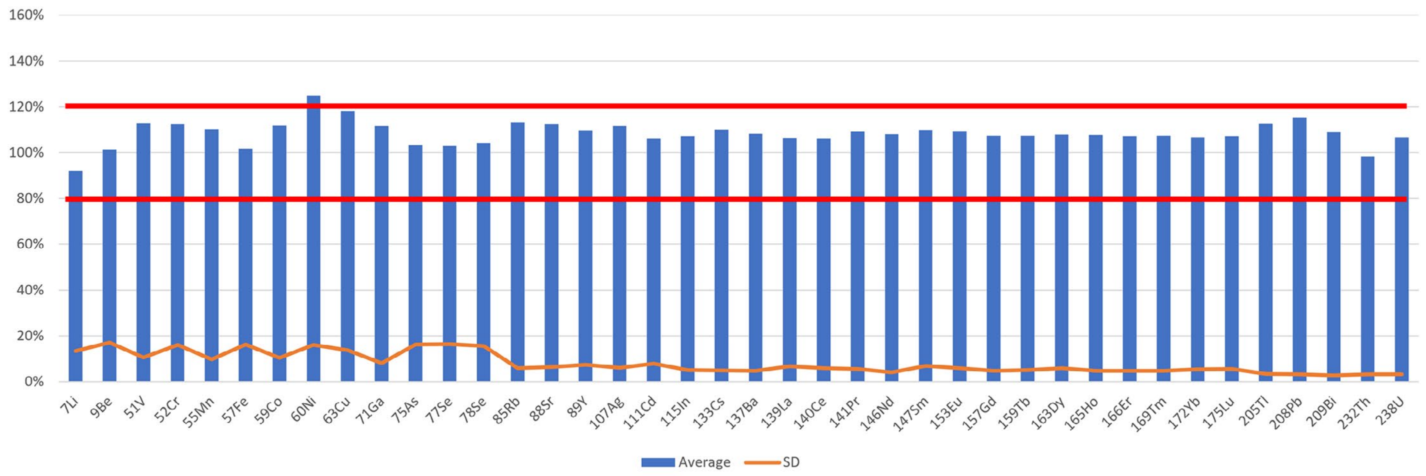

Figure 1. Average recovery of all analytes in a QC sample, periodically analyzed during the entire sequence (N=7)

Accuracy test

To verify the accuracy of the results, a spike recovery test was performed for four out of the 10 samples under investigation. Therefore, all samples were spiked with a concentration of 2 μg·L^{-1} for most analytes except major elements Na, Mg, and K and the rare earth elements (Y, Th, Lanthanides), which were spiked with 0.1 μg·L^{-1}. The results are summarized in Figure 2. In some cases, results had to be eliminated as the concentration naturally present in the samples was too high to yield a quantifiable difference to the spiked amount. But generally, all elements typically found in trace level amounts returned acceptable recoveries between 80% and 120%.

As can be seen from the data summarized in Table 3, there are differences in concentrations of various analytes under investigation. The major influencing factor for the overall amount in the production of whisky is the raw ingredients, i.e., grains and water used for fermentation. Whereas major elements like sodium, magnesium, potassium, or calcium are present in elevated concentrations, it is important to note that for use as a tracer they might be inappropriate due to the higher risk of contamination. However, heavier homologues of the alkaline and alkaline earth elements may be potential indicators. Similarly, the concentrations of lanthanide elements will be influenced by the geological conditions of the soil in which the grains used in the fermentation process were grown. Finally, process equipment during the distillation may also contribute to overall presence and concentration levels of common transition metals, such as for example vanadium, chromium, manganese, iron, or copper.

To potentially distinguish the samples from one another, it is important to ensure that the differences in concentration are sufficiently different. To evaluate the results, box whisker plots were generated for selected elements and are shown in Figure 3.

Amongst all analytes, copper shows the highest variation between individual samples (10.7 to 1,641 μg·L^{-1}). Along with copper, variations in other transition metals can be observed, which may point to material-specific differences incurred from the distillation process. For example, samples 1 and 8 showed significant deviations in the levels of vanadium (elevated significantly versus all other samples in sample number 8) and chromium (in sample 1). One of the samples with undefined origin (sample 8) contained significantly higher values for all lanthanide group elements, exceeding all other samples significantly for almost all homologs of the series. Higher homologs of the alkaline and alkaline earths as such seem to not show major differences for whiskies from either of the regions (nor in between them), with the exception of sample 7, which clearly showed the lowest amount of barium (versus all other samples), but a significantly higher level of cesium.

A specific difference in the levels of arsenic was also observed between samples 1 to 6 and 7 to 10, respectively (average content 12.1 μg·L^{-1} versus 0.5 μg·L^{-1}). This could potentially be caused by different geological features amongst the regions of origin. However, the reason for this observation could also be related to the material of the vessels in which the samples have been shipped. Since no blanks were provided for analysis, leaching of arsenic cannot be excluded.

Table 3. Results obtained for all samples. All results are given in µg·L^{-1} in the original sample, hence considering the four-fold dilution during sample preparation. N = 3 individual readings per sample were averaged.

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
^{7}Li	0.50 ± 0.08	1.21 ± 0.17	0.55 ± 0.12	2.3 ± 0.2	0.47 ± 0.02	0.16 ± 0.03	1.78 ± 0.21	1.61 ± 0.05	0.70 ± 0.05	0.61 ± 0.11
^{9}Be	n.d.	n.d.	≤ 0.01	0.028 ± 0.011	0.035 ± 0.025	n.d.	n.d.	0.49 ± 0.06	n.d.	n.d.
^{23}Na	9,900 ± 600	7760 ± 308	6082 ± 134	7323 ± 197	15,892 ± 306	9949 ± 208	12,676 ± 338	1760 ± 59	11,888 ± 508	4146 ± 102
^{24}Mg	238 ± 17	212 ± 10	315 ± 9	934 ± 22	274 ± 9	169 ± 7	354 ± 13	341 ± 13	243 ± 15	314 ± 10
^{39}K	9285 ± 688	9526 ± 447	7675 ± 113	23,020 ± 867	8182 ± 136	4265 ± 125	7496 ± 248	20,151 ± 542	6557 ± 281	9600 ± 212
^{44}Ca	707 ± 5	548 ± 16	968 ± 26	1679 ± 60	1103 ± 24	786 ± 12	1345 ± 44	1414 ± 34	826 ± 25	1131 ± 24
^{51}V	0.18 ± 0.008	0.043 ± 0.002	0.52 ± 0.02	0.59 ± 0.02	0.45 ± 0.02	0.12 ± 0.01	0.17 ± 0.02	8.78 ± 0.48	0.26 ± 0.02	0.12 ± 0.1
^{52}Cr	9.94 ± 0.81	0.46 ± 0.04	0.54 ± 0.02	1.45 ± 0.03	1.15 ± 0.05	1.08 ± 0.02	1.08 ± 0.04	3.26 ± 0.20	0.89 ± 0.09	0.33 ± 0.05
^{55}Mn	20.8 ± 1.5	15.6 ± 0.7	21.7 ± 0.5	40.3 ± 1.3	22.9 ± 0.6	32.4 ± 0.8	23.2 ± 0.7	67.3 ± 2.5	21.3 ± 1.0	47.4 ± 1.2
^{57}Fe	58.2 ± 3.7	48.5 ± 1.7	32.8 ± 0.8	320.5 ± 6.7	94.0 ± 2.8	30.3 ± 0.6	32.8 ± 1.9	109.2 ± 7.9	175.8 ± 10.7	17.4 ± 0.8
^{59}Co	0.148 ± 0.007	0.031 ± 0.002	0.83 ± 0.02	0.376 ± 0.004	0.21 ± 0.01	0.077 ± 0.002	0.071 ± 0.002	0.32 ± 0.02	0.077 ± 0.005	0.089 ± 0.005
^{60}Ni	1.29 ± 0.08	212 ± 37	1.75 ± 0.35	2.75 ± 0.34	1.42 ± 0.06	1.66 ± 0.11	2.64 ± 0.06	3.70 ± 0.15	1.56 ± 0.08	1.25 ± 0.08
^{63}Cu	539.7 ± 33.7	767 ± 38	132.6 ± 2.8	1112 ± 26	334.1 ± 9.5	232.4 ± 4.0	1641 ± 56	24.4 ± 1.2	10.7 ± 0.6	629.5 ± 18.7
^{71}Ga	n.d.	n.d.	≤0.01	0.055 ± 0.006	0.031 ± 0.006	0.029 ± 0.005	≤0.01	0.18 ± 0.01	0.028 ± 0.004	n.d.
^{75}As	10.7 ± 0.8	9.8 ± 0.4	8.7 ± 0.2	14.3 ± 1.2	15.8 ± 0.6	13.6 ± 0.3	0.43 ± 0.02	1.19 ± 0.05	0.21 ± 0.03	0.12 ± 0.01
^{78}Se	0.12 ± 0.02	0.18 ± 0.06	0.11 ± 0.06	0.17 ± 0.06	0.16 ± 0.06	0.11 ± 0.04	0.34 ± 0.05	0.26 ± 0.05	0.15 ± 0.07	0.11 ± 0.03
^{85}Rb	11.5 ± 0.6	14.5 ± 0. 6	8.1 ± 0.1	25.1 ± 1.0	9.3 ± 0.2	7.6 ± 0.2	8.5 ± 0.2	25.5 ± 0.5	7.6 ± 0.1	11.1 ± 0.4
^{88}Sr	2.75 ± 0.13	2.68 ± 0.11	5.07 ± 0.10	7.79 ± 0.28	4.83 ± 0.06	3.76 ± 0.10	5.59 ± 0.18	24.9 ± 0.3	3.5 ± 0.1	3.3 ± 0.1
^{89}Y	0.033 ± 0.002	≤0.01	0.168 ± 0.004	0.113 ± 0.002	0.136 ± 0.004	0.027 ± 0.002	0.139 ± 0.006	1.96 ± 0.05	0.183 ± 0.002	0.023 ± 0.002
^{107}Ag	n.d.	≤ 0.01	n.d.	≤ 0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
^{111}Cd	n.d.	0.052 ± 0.008	n.d.	n.d.	n.d.	n.d.	n.d.	0.075 ± 0.002	n.d.	n.d.
^{115}In	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.35 ± 0.02	n.d.	n.d.	n.d.
^{133}Cs	0.100 ± 0.004	0.072 ± 0.004	0.067 ± 0.002	0.067 ± 0.002	0.061 ± 0.005	0.089 ± 0.002	11.3 ± 0.3	0.111 ± 0.002	0.077 ± 0.002	0.069 ± 0.005
^{137}Ba	42.0 ± 1.6	37.8 ± 1.3	45.9 ± 0.4	30.1 ± 1.3	39.2 ± 0.7	43.3 ± 1.3	4.74 ± 0.08	14.7 ± 0.1	24.2 ± 0.4	2.17 ± 0.07
^{139}La	0.034 ± 0.002	0.017 ± 0.002	0.051 ± 0.002	0.139 ± 0.002	0.095 ± 0.002	0.027 ± 0.002	≤0.01	0.64 ± 0.02	0.157 ± 0.005	0.016 ± 0.001
^{140}Ce	0.085 ± 0.003	0.035 ± 0.002	0.050 ± 0.002	0.239 ± 0.008	0.163 ± 0.002	0.092 ± 0.004	0.017 ± 0.002	1.38 ± 0.02	0.220 ± 0.008	0.039 ± 0.002
^{141}Pr	n.d.	≤0.01	≤0.01	0.034 ± 0.002	0.024 ± 0.001	≤0.01	n.d.	0.1777 ± 0.005	0.043 ± 0.002	n.d.
^{146}Nd	0.037 ± 0.002	≤0.01	≤0.01	0.143 ± 0.005	0.100 ± 0.004	0.025 ± 0.002	≤0.01	0.780 ± 0.004	0.173 ± 0.002	0.027 ± 0.002
^{147}Sm	≤0.01	≤0.01	0.025 ± 0.002	0.029 ± 0.002	0.020 ± 0.001	≤0.01	≤0.01	0.189 ± 0.006	0.035 ± 0.002	n.d.
^{153}Eu	≤0.01	n.d.	≤0.01	≤0.01	≤0.01	≤0.01	n.d.	0.031 ± 0.002	≤0.01	n.d.
^{157}Gd	≤0.01	≤0.01	0.024± 0.002	0.027 ± 0.002	0.020 ± 0.001	≤0.01	n.d.	0.229 ± 0.002	0.035 ± 0.002	n.d.
^{159}Tb	≤0.01	n.d.	n.d.	≤0.01	n.d.	n.d.	n.d.	0.036 ± 0.001	≤0.01	n.d.
^{163}Dy	n.d.	≤0.01	0.024± 0.002	≤0.01	0.017 ± 0.002	≤0.01	n.d.	0.224 ± 0.004	0.031 ± 0.002	n.d.
^{165}Ho	n.d.	n.d.	n.d.	≤ 0.01	≤ 0.01	n.d.	n.d.	0.047 ± 0.002	≤0.01	n.d.
^{166}Er	≤0.01	n.d.	0.020± 0.002	≤0.01	≤0.01	≤0.01	n.d.	0.135 ± 0.002	0.028 ± 0.002	n.d.
^{169}Tm	n.d.	n.d.	n.d.	≤0.01	≤0.01	n.d.	n.d.	0.019 ± 0.002	≤0.01	n.d.
^{172}Yb	≤0.01	n.d.	0.021± 0.002	≤0.01	≤0.01	≤0.01	n.d.	0.112 ± 0.004	0.016 ± 0.001	n.d.
^{175}Lu	n.d.	n.d.	n.d.	≤0.01	≤0.01	n.d.	n.d.	0.016 ± 0.001	≤0.01	n.d.
^{205}Tl	0.027± 0.002	≤0.01	0.019± 0.002	0.029 ± 0.002	0.020± 0.002	0.024± 0.002	≤0.01	≤0.01	≤0.01	n.d.
^{208}Pb	0.98 ± 0.01	2.22 ± 0.08	0.385 ± 0.002	1.81 ± 0.01	1.21 ± 0.02	1.84 ± 0.05	0.69 ± 0.01	0.51 ± 0.1	0.34 ± 0.1	0.112 ± 0.004
^{209}Bi	0.016 ± 0.003	≤0.01	≤0.01	≤0.01	≤0.01	0.027 ± 0.002	0.021 ± 0.002	≤0.01	≤0.01	n.d.
^{232}Th	≤0.01	n.d.	≤0.01	≤0.01	≤0.01	≤0.01	n.d.	0.060 ± 0.004	n.d.	n.d.
^{238}U	≤0.01	≤0.01	≤0.01	0.083 ± 0.002	0.045 ± 0.002	0.013 ± 0.002	≤0.01	0.123 ± 0.002	0.028 ± 0.001	0.028 ± 0.001

n.d. – not detected (below method detection limit)

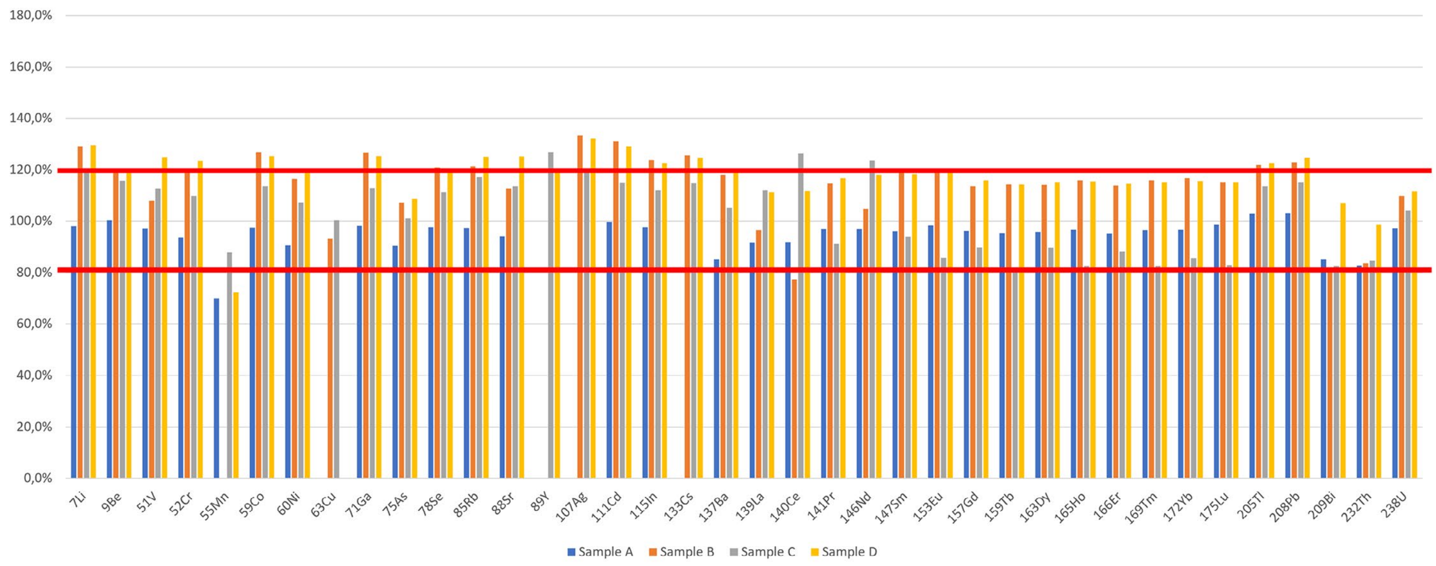

Figure 2. Results of the spike recovery test. N=5 readings were averaged.

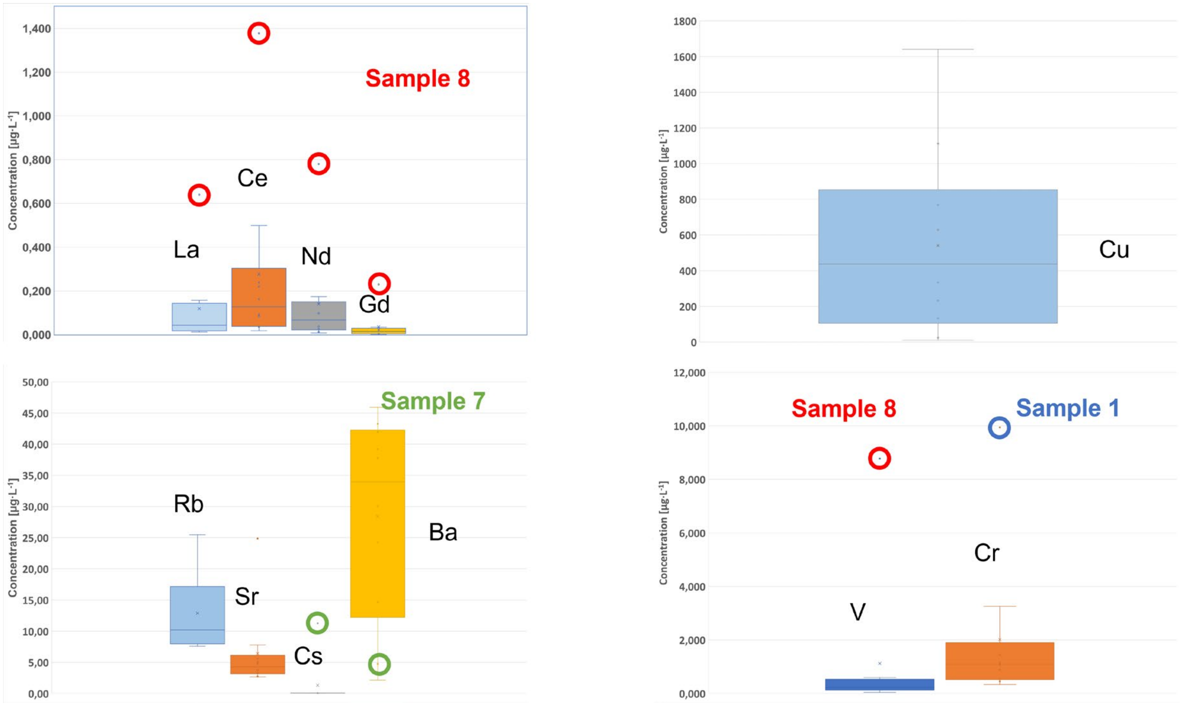

Figure 3. Box plots representing the concentration of selected elements across all samples

Conclusion

This study demonstrates that whisky, as well as other alcoholic beverages, can be analyzed for its complete trace elemental profile using the iCAP MSX ICP-MS following a simple dilution. The high robustness of the plasma as well as the re-designed sample introduction system allows solutions containing approximately 10 vol% of EtOH to be aspirated. Only minor changes to the sample introduction configuration were made to maximize sensitivity and account for the expected lower nebulizer flow rate. The data specifically demonstrates the high sensitivity of the instrument and its ability to remove polyatomic interferences. This in turn can be used to detect a wide range of elements that may show variability in whisky (and potentially other spirits derived from fermented agricultural products) based on geological conditions and/or processing materials or equipment used.

Reference

1. Application Note 3094: Whisky profiling using non-target analysis with headspace Arrow solid phase microextraction with high resolution accurate mass (HRAM) spectrometry; Thermo Fisher Scientific.

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