Trace elemental analysis of distilled alcoholic beverages using the Agilent 7700x ICP-MS with octopole collision/reaction cell

Application note

Food testing

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Abstract

A method is described for the measurement of trace elements in alcoholic beverages including bourbon, rum, liqueur, sake, vodka, Irish whiskey and Scottish whisky, using an Agilent 7700x ICP-MS featuring the Octopole Reaction System (ORS^3). The 7700x ensures simple operation as a single method and single set of conditions can be used to measure all sample types, following a simple dilution. Excellent spike recoveries were obtained, demonstrating the ability of the ORS^3 in helium mode to remove interferences regardless of their source. The study shows that the 7700x can be used for the routine measurement of trace metals in alcoholic beverages.

Introduction

The measurement of trace elements in alcoholic beverages is required from a quality control standpoint and also to ensure that the final product complies with any regulatory requirements. Metal content can originate from the raw ingredients, such as water or grain, as well as during processing, for example from fermentation or distillation equipment. An example would be high arsenic concentration from distillation vessels manufactured from poor quality copper. The levels of trace elements can also significantly affect the taste of the product. Consequently, there is a requirement to measure elemental concentrations in the final product. While ICP-MS offers high sensitivity and excellent detection limits for many elements, interferences on key elements arising from the carbon content and required sample preparation can be problematic.

The Agilent 7700x ICP-MS features the Octopole Reaction System (ORS^3) collision/reaction cell, which removes matrix-based polyatomic interferences using a single set of cell conditions (helium collision mode). For the analysis of spirits, the major interferences resulting from the sample matrix would be carbon-based (for example, $^{40}Ar^{12}C$ on ^{52}Cr). Many elements are much more stable in a chloride matrix than after simple acidification using nitric acid; for this reason, hydrochloric acid (HCl) was added to the samples at a final concentration of 0.5%. New interferences are created by the addition of HCl (for example, $^{35}Cl^{16}O$ on ^{51}V; $^{40}Ar^{35}Cl$ on ^{75}As, and so forth) but they are also removed by the ORS^3 in helium mode (He mode).

Experimental

Sample preparation and instrument conditions

Samples were prepared by a simple 5x dilution using 1% HNO_3 and 0.5% HCl (v/v). Using an acid mix significantly improves the stability of many elements, particularly Hg. In order to compensate for sample transport effects and solvent evaporation rates, the alcohol content of the standards was matched to that of the samples by adding ~10% ethanol to all standard solutions (approximately equivalent to 5x dilution of the original samples, which contained ~40% v/v alcohol). This also compensates for ionization enhancement effects for As and Se in the presence of high carbon concentrations. Internal standards were added on-line and no further matrix matching was necessary. As no reference materials are available for these matrices, spike recoveries were performed on several samples.

All measurements were performed using a standard Agilent 7700x ICP-MS fitted with the standard sample introduction system consisting of a MicroMist glass concentric nebulizer, quartz Scott-type Peltier-cooled spray chamber, Ni interface cones and ORS^3 operating under He mode or without cell gas (no gas mode). The optional hydrogen mode was not required. Instrument conditions are displayed in Table 1.

Table 1. Agilent 7700x ICP-MS operating conditions

Parameter	Value
Forward power	1550 W
Carrier gas flow rate	0.8 L/min
Make-up gas flow rate	0.32 L/min
Spray chamber temperature	2 °C
Sampling depth	8.0 mm
ORS^3 helium gas flow rate	5.0 mL/min

Data acquisition

Data was acquired operating the ORS^3 in He mode and no gas mode. Some elements were acquired in both modes for comparison purposes to highlight the efficiency of He mode for interference removal.

He mode is the default mode of operation of the 7700x. The inert He cell gas conditions remove interferences based upon their ionic cross-section rather than relying on a reactive gas. As almost all interferences in ICP-MS are polyatomic in nature, they possess a greater ionic cross-section than the monatomic analyte ion at the same mass and therefore undergo a greater number of collisions in the cell. As each collision causes energy loss, the interfering polyatomic ions lose more energy than the analyte ions and are subsequently filtered from the mass-spectrum by discriminating between the two different energies (called kinetic energy discrimination). Since this process takes place regardless of the analyte-interferent combination, and works for multiple polyatomic ion overlaps at each analyte mass, a single set of conditions can be used for all analytes.

Results and discussion

Detection limits (DL) and background equivalent concentrations (BEC) are presented in Table 2. Some elements were acquired both without cell gas (no gas) and in He mode for comparison. For those elements that suffer from interferences in this carbon and chloride matrix, the BECs and DLs are severely compromized when operating the instrument in no gas mode (that is, conventional non-cell ICP-MS). This can be clearly observed in the data for chromium: The BEC for ^{52}Cr without cell gas (no gas mode) was 162.8 µg/L compared to 0.0117 µg/L in He mode — an improvement of more than 4 orders of magnitude. The interference is effectively reduced to background contamination levels as the BECs for both Cr isotopes are very similar. Improvements can also be observed for Mg, Al, Ca, V, Mn, Fe, As and Se — all of which were measured in He mode.

Figure 1 shows the calibration graphs for ^{9}Be, ^{51}V, ^{24}Mg, ^{52}Cr, ^{53}Cr and ^{238}U. There are two calibration graphs for those elements that suffer from interferences (^{24}Mg, ^{51}V, ^{52}Cr, ^{53}Cr). One was acquired in no gas mode (without cell gas) and one in He mode. The 'no gas' calibrations for Cr do not pass through the origin due to the carbon and chlorine-based interferences and this offset can be clearly seen. There is an improvement in the BEC and DL in the calibrations for ^{24}Mg, ^{51}V, ^{52}Cr, and ^{53}Cr in He mode. Be and U are also presented to demonstrate the excellent sensitivity for these low and high mass elements.

In order to obtain the lowest possible detection limits, it is essential to maximize the ionization efficiency of the plasma. This is done through optimization of the sample introduction system (low solution and gas flow rates and wide bore injector torch, temperature controlled spray chamber) and plasma generator design (27.12 MHz, solid-state with high coupling efficiency digital drive). All of these factors combine to increase the effective central channel temperature, improving ionization efficiency. This is allied to an ion lens system designed to improve full-mass ion transmission efficiency, further improving the DLs.

Table 2. Background equivalent concentration (BEC) and 3σ detection limits (µg/L) for a blank matrix containing 10% ethanol, 1% HNO_3 and 0.5% HCl in He mode and without cell gas (no gas mode).
* Some examples of plasma and matrix based interferences are also presented for information.

Mode	Mass/ Element	Interference*	3σ DL (µg/L)	BEC (µg/L)
No gas	^{9}Be		0.00019	0.00056
No gas	^{23}Na		0.406	8.82
No gas	^{24}Mg	$^{12}C_2$	1.25	10.18
He	^{24}Mg		0.118	0.608
No gas	^{27}Al	^{12}C^{15}N; ^{13}C^{14}N	0.133	1.36
He	^{27}Al		0.023	0.558
He	^{39}K	^{40}Ar^{1}H	2.393	23.09
No gas	^{44}Ca	$^{12}C^{16}O_2$	152.1	1902.9
He	^{44}Ca		2.36	3.40
No gas	^{51}V	^{37}Cl^{16}O; ^{37}Cl^{14}N; ^{38}Ar^{13}C	0.125	1.35
He	^{51}V		0.00099	0.0049
No gas	^{52}Cr	^{40}Ar^{12}C; ^{36}Ar^{16}O; ^{35}Cl^{17}O; ^{37}Cl^{15}N	6.49	162.8
He	^{52}Cr		0.0117	0.067
No gas	^{53}Cr	^{40}Ar^{13}C; ^{37}Cl^{16}O	1.32	20.92
He	^{53}Cr		0.0387	0.0461
No gas	^{55}Mn	^{40}Ar^{15}N	0.0569	0.157
He	^{55}Mn		0.0590	0.033
No gas	^{56}Fe	^{40}Ar^{16}O	4.55	56.17
He	^{56}Fe		0.265	0.326
He	^{59}Co		0.00088	0.00069
He	^{60}Ni		0.0148	0.177
He	^{63}Cu		0.0106	0.098
He	^{65}Cu		0.0104	0.101
He	^{66}Zn		0.0124	0.118
No gas	^{75}As	^{40}Ar^{35}Cl	0.0064	0.412
He	^{75}As		0.0013	0.0018
No gas	^{78}Se	^{40}Ar^{38}Ar	0.559	2.495
He	^{78}Se		0.0059	0.0038
No gas	^{88}Sr		0.00083	0.0049
No gas	^{95}Mo		0.0023	0.0047
No gas	^{107}Ag		0.00061	0.0118
He	^{111}Cd		0.0013	0.00078
No gas	^{121}Sb		0.00081	0.0014
No gas	^{138}Ba		0.00041	0.0042
He	^{201}Hg		0.0012	0.0036
No gas	^{205}Tl		0.0014	0.0038
No gas	^{208}Pb		0.00086	0.0088
No gas	^{238}U		0.00014	0.00024

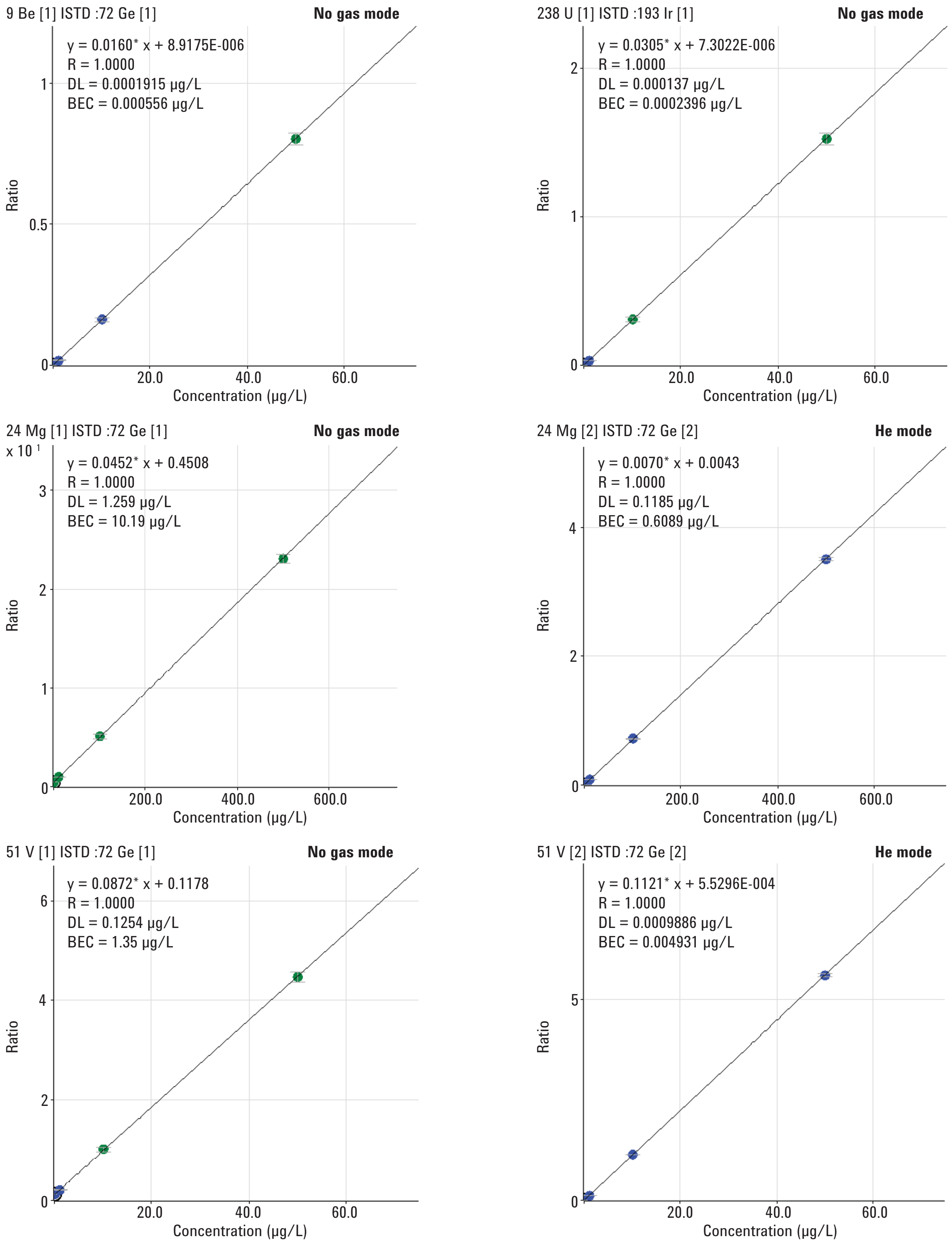

Figure 1. Calibration graphs for Be (no gas), U (no gas), Mg (no gas), Mg (He), V (no gas) and V (He). Masses/elements suffering from carbon and chlorine-based interferences can clearly be observed in no gas mode. (Continued next page)

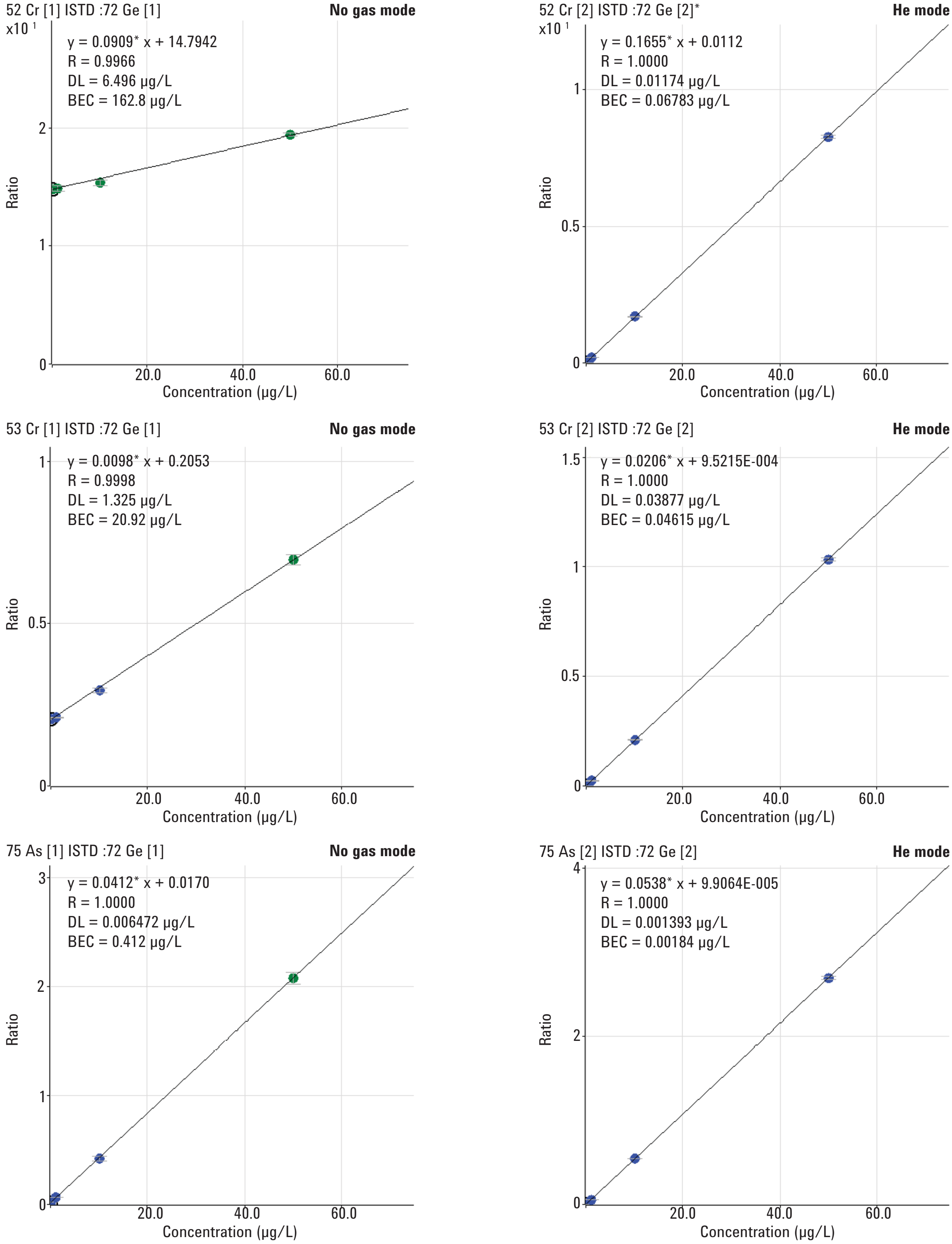

Figure 1. (Continued) Calibration graphs for ^{52}Cr (no gas), ^{52}Cr (He), ^{53}Cr (no gas), ^{53}Cr (He), As (no gas), and As (He). Masses/elements suffering from carbon and chlorine-based interferences can clearly be observed in no gas mode.

The elements Ge, Rh, and Ir were used as internal standards and were added on-line.

Tables 3, 4 and 5 display the quantitative data for all samples, including a spike recovery for a bourbon sample (Table 3) and spike recoveries for two of the Irish whiskey samples (Table 4). Data are displayed in the preferred cell gas mode (usually helium). The recovery limits for all spiked elements were well within the range 80–120%, indicating good accuracy. Only the recovery for K in Sample 2 of the Irish whiskey sample set was outside of this range. Because K is present at a high natural level in the sample, a higher spike level would be preferred. Results for both Cr and Cu isotopes in all samples show good agreement, which is a good indication that all interferences on both isotopes were effectively removed.

Table 3. Analytical results (µg/L) and spike recoveries for a range of spirit beverages. Due to the distillation process many elements are present at sub-ppb concentrations.

	Bourbon					**Other**			
Element/Mode	**Sample A**	**Sample B**	**Sample C**	**Spike**	**% Recovery**	**Rum**	**Liqueur**	**Sake**	**Vodka**
^{9}Be /no gas	0.00050	0.00143	0.00420	9.661	96.6	0.00028	0.00039	0.00080	0.00101
^{23}Na /no gas	5894.3	7109.8	297.3	408.6	111.3	162.8	625.5	962.3	200.9
^{24}Mg /He	3.9	83.6	31.8	135.2	103.4	6.8	416.2	344.8	8.0
^{27}Al /He	0.8	6.3	10.1	19.6	94.8	1.3	1.6	19.1	0.3
^{39}K /He	381.5	2109.4	2157.4	2275.4	118.0	0.7	1087.1	419.3	23.0
^{44}Ca /He	8.8	30.9	18.2	109.6	91.5	8.8	686.8	330.5	21.0
^{51}V /He	0.009	0.692	0.137	9.578	94.4	0.008	0.078	0.101	0.017
^{52}Cr /He	0.01	0.21	0.17	9.62	94.5	0.07	0.13	0.03	0.00
^{53}Cr /He	0.01	0.19	0.16	9.64	94.8	0.05	0.08	0.04	0.00
^{55}Mn /He	0.49	1.24	8.71	18.37	96.6	0.32	0.86	9.73	0.12
^{56}Fe /He	1.09	29.19	4.88	95.70	90.8	31.35	1.94	5.05	0.32
^{59}Co /He	0.016	0.020	0.025	8.936	89.1	0.006	0.017	0.105	0.004
^{60}Ni /He	0.047	0.116	0.214	9.844	96.3	0.124	0.021	0.016	0.029
^{63}Cu /He	0.83	1.97	32.88	44.23	113.5	304.54	1.50	3.11	1.77
^{65}Cu /He	0.89	2.11	35.06	44.75	96.9	326.49	1.59	3.33	1.90
^{66}Zn /He	0.46	1.59	1.75	11.70	99.5	6.64	14.63	0.90	2.36
^{75}As /He	0.0051	0.2312	0.0346	9.609	95.7	0.0112	0.0477	0.0838	0.0027
^{78}Se /He	0.0049	0.0518	0.0071	10.46	104.6	0.0097	0.0113	0.0433	0.0052
^{88}Sr /No gas	0.11	1.10	0.39	10.61	102.2	0.09	10.13	7.76	0.31
^{107}Ag /no gas	0.005	0.001	0.003	9.576	95.7	0.003	0.001	0.002	0.007
^{111}Cd /He	0.0039	0.0053	0.0193	9.811	97.9	0.0115	0.0227	0.0016	0.0040
^{121}Sb /no gas	0.027	0.057	0.012	10.994	109.8	0.008	0.137	0.010	0.015
^{138}Ba /no gas	0.070	0.343	0.260	10.250	99.9	0.004	0.738	0.372	1.342
^{201}Hg /He	0.0034	0.0019	0.0004	0.200	100.0	0.0038	0.0026	0.0001	0.0089
^{205}Tl /no gas	0.0007	0.0009	0.0013	10.224	102.2	0.0016	0.0008	0.0021	0.0004
^{208}Pb /no gas	0.021	0.088	0.862	10.022	91.6	0.776	0.062	0.054	0.013
^{238}U /no gas	0.001	0.011	0.003	10.223	102.2	0.000	0.047	0.063	0.002

Table 4. Analytical results (µg/L) and spike recoveries for three Irish whiskey samples. Due to the distillation process many elements are present at sub-ppb concentrations.

Element/Mode	Sample A	Spike	% Recovery	Sample B	Spike	% Recovery	Sample C
^{9}Be /no gas	0.00085	9.227	92.3	0.00389	9.437	94.3	0.00369
^{23}Na /no gas	778.6	887.2	108.6	1018.0	1114.3	96.3	623.6
^{24}Mg /He	5.4	103.9	98.4	21.1	120.5	99.5	47.3
^{27}Al /He	2.0	11.7	97.6	6.1	15.0	89.8	8.5
^{39}K /He	381.2	485.5	104.4	931.8	1004.2	72.4	1529.3
^{44}Ca /He	6.8	106.1	99.3	22.2	117.2	95.1	32.7
^{51}V /He	0.025	9.824	98.0	0.047	9.467	94.2	0.063
^{52}Cr /He	0.68	10.49	98.2	0.67	10.10	94.3	0.82
^{53}Cr /He	0.65	10.40	97.5	0.66	10.05	93.9	0.81
^{55}Mn /He	0.63	10.42	97.9	2.54	11.84	93.0	2.74
^{56}Fe /He	1.53	100.38	98.9	6.04	99.19	93.1	10.81
^{59}Co /He	0.007	9.136	91.3	0.049	8.870	88.2	0.032
^{60}Ni /He	0.028	9.798	97.7	0.048	9.510	94.6	0.002
^{63}Cu /He	0.90	10.19	92.8	3.33	12.27	89.4	3.51
^{65}Cu /He	0.97	10.88	99.1	3.54	13.03	95.0	3.76
^{66}Zn /He	0.10	10.43	103.3	0.31	10.10	97.8	0.76
^{75}As /He	0.0069	9.5975	95.9	0.0202	9.2482	92.3	0.0140
^{78}Se /He	0.0035	9.6230	96.2	0.0049	9.7909	97.9	0.0050
^{88}Sr /no gas	0.10	9.71	96.1	0.46	10.19	97.3	1.09
^{107}Ag /no gas	0.001	9.056	90.6	0.005	9.337	93.3	0.001
^{111}Cd /He	0.0011	9.9280	99.3	0.0017	9.6625	96.6	0.0022
^{121}Sb /no gas	0.011	8.903	88.9	0.014	8.899	88.8	0.013
^{138}Ba /no gas	0.069	9.653	95.8	1.702	11.496	97.9	0.386
^{201}Hg /He	0.0021	0.1886	93.3	0.0040	0.1967	96.4	0.0022
^{205}Tl /no gas	0.0010	9.3196	93.2	0.0031	9.9106	99.1	0.0002
^{208}Pb /no gas	0.030	8.660	86.3	0.064	9.044	89.8	0.132
^{238}U /no gas	0.004	9.558	95.5	0.010	9.982	99.7	0.007

Table 5. Analytical results (µg/L) for four Scottish whisky samples. Due to the distillation process many elements are present at sub-ppb concentrations.

Element/Mode	Sample A	Sample B	Sample C	Sample D
^{9}Be /no gas	0.01417	0.00574	0.00345	0.00103
^{23}Na /no gas	935.6	1333.2	1070.6	883.9
^{24}Mg /He	41.2	30.3	16.0	18.8
^{27}Al /He	13.9	19.5	6.4	6.8
^{39}K /He	668.0	673.3	474.6	607.0
^{44}Ca /He	36.4	24.0	12.4	16.5
^{51}V /He	0.156	0.038	0.056	0.028
^{52}Cr /He	0.11	0.14	0.11	0.07
^{53}Cr /He	0.11	0.14	0.10	0.07
^{55}Mn /He	5.01	3.01	1.39	1.02
^{56}Fe /He	9.56	7.43	5.73	11.14
^{59}Co /He	0.102	0.035	0.019	0.008
^{60}Ni /He	0.261	0.125	0.056	0.004
^{63}Cu /He	52.49	31.84	46.23	24.05
^{65}Cu /He	52.39	33.91	45.10	25.60
^{66}Zn /He	1.93	1.68	0.82	1.38
^{75}As /He	0.0467	0.0393	0.0265	0.0214
^{78}Se /He	0.0262	0.0312	0.0179	0.0093
^{88}Sr /no gas	0.86	0.63	0.19	0.26
^{107}Ag /no gas	0.005	0.003	0.002	0.000
^{111}Cd /He	0.0038	0.0022	0.0014	0.0020
^{121}Sb /no gas	0.018	0.011	0.011	0.010
^{138}Ba /no gas	0.404	0.318	0.219	0.152
^{201}Hg /He	0.0026	0.0014	0.0005	0.0019
^{205}Tl /no gas	0.0004	0.0010	0.0014	0.0015
^{208}Pb /no gas	0.131	0.107	0.111	0.167
238U /no gas	0.030	0.005	0.006	0.002

Conclusions

Routine analysis of alcoholic spirit beverages using the Agilent 7700x ICP-MS was performed following a simple sample dilution/acidification. No sample-specific method development or customized cell modes were required, as the use of helium gas mode in the ORS^{3} of the 7700x efficiently removed the plasma-based and matrix-based interferences from all analytes. He mode improves detection limits and ensures accurate and reliable results with a simple, consistent set of conditions for all interfered elements, regardless of the sample composition. He mode provides improvements in detection limits of around 4 orders of magnitude and is applicable to multielement analysis in a wide range of sample types.

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