Measurement of Trace Elements in Malt Spirit Beverages (Whisky) by 7500cx ICP-MS

Application

Food

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Abstract

A method for the measurement of trace elements in malt spirits (whisky) is described with reference to six different samples. An Agilent 7500cx ICP-MS featuring the Octopole Reaction System (ORS) was used for the analysis. The 7500cx ensures simple operation as a single method and a single set of conditions can be used to remove interferences regardless of their source. Excellent spike recoveries were obtained (between 97 and 107%) following a simple dilution of the samples. A 5-hour stability test yielded excellent precision (< 2%) for almost all elements. The study shows that the 7500cx can be used for the routine measurement of trace metals in 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 whisky. 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 alcohol content and required sample preparation can be problematic.

The 7500cx features the Octopole Reaction System (ORS) collision/reaction cell, which removes matrix-based polyatomic interferences using a single set of cell conditions (helium mode). For the analysis of spirits, the major interferences resulting from the sample would be carbon-based (for example, $^{40}Ar^{12}C$ on ^{52}Cr). Many elements are much more stable in a chloride matrix than simple acidification using nitric acid; for this reason, hydrochloric acid (HCl) was added to the samples. 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, etc.) but they are removed by the ORS in helium mode.

An optional cell gas line is available for the 7500cx, enabling operation in hydrogen (H_2) reaction mode, which allows for the measurement of selenium at ultratrace levels. Since several of the solutions contained less than 40 ng/L Se (some significantly lower than this) in solution after dilution, H_2 reaction mode was also used during this study.

Experimental

Sample Preparation & Instrumental Conditions

Four Scottish whiskies (Highland, Speyside, Islay, and a blend), one Irish whisky, one U.S. bourbon –

as well as a further Scottish whisky and a U.S. bourbon that had been stored in lead crystal decanters – were analyzed. The samples were prepared by 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 and Sn, compared to the use of nitric acid alone. Standards were prepared from 1,000 ppm stock single-element solutions to produce final mixed-element calibration solutions. 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 8% ethanol to all standard solutions (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. Gold (400 µg/L) was also added to the standards and samples in order to further improve the stability of Hg.

Table 1 lists the instrumental conditions used for the analysis; sample uptake rate was approximately 150 µL/min and sampling was facilitated by the Agilent ASX-520 autosampler. The solution pump program was optimized using the preemptive rinse function in the ChemStation software in addition to a multichemistry rinse regime [1]. The 7500cx was operated under standard conditions, and internal standards (Ge, Rh, and Ir) were added automatically on line by the system's peristaltic pump. No special precautions were necessary for these sample types.

Table 1. Agilent 7500cx Operating Conditions

RF power	1550 W
Sampling depth	8 mm
Carrier gas flow	0.68 L/min
Makeup gas flow	0.33 L/min
Spray chamber temperature	15 °C
Helium cell gas flow	5.5 mL/min
Hydrogen cell gas flow	4.0 mL/min

Data Acquisition

Data was acquired operating the ORS in helium [He], hydrogen [H_2], and no-gas modes. Helium mode is the default mode of operation of the 7500cx. The inert He cell gas conditions remove interferences based on 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 cross-section than the monatomic analyte at the same mass and therefore undergo a greater number of collisions in the cell. As each collision causes energy loss, the interfering species lose more energy than the analyte and are subsequently filtered from the mass spectrum by discriminating between the two different energies (called energy discrimination). As this process takes place regardless of the analyte-interference combination, a single set of conditions can be used for all analytes.

Selenium was measured in hydrogen mode as the concentration of this element in the diluted sample was at low ppt levels. Although selenium can be measured in helium mode, hydrogen mode removes the Ar-based interference with greater efficiency, improving the detection limit for this element, and is the better option for low-ppt concentrations. Some isotopes were determined in both helium mode and no-gas mode to provide comparative data on cell performance. For routine analysis this would not be necessary, of course. All cell modes were acquired within a single acquisition and sample pass.

Results and Discussion

Table 2 summarizes the detection limits (DLs), background equivalent concentrations (BECs), and calibration regression for the isotopes studied in the different cell modes (default mode is highlighted in bold typeface). For those elements that suffer from interferences in this carbon and chloride matrix, BECs and DLs are severely compromised when operating the instrument in no-gas mode (that is, conventional ICP-MS). This can be clearly observed in the data for chromium: ^{52}Cr BEC without cell gas is 526 µg/L, and in helium mode is 0.07 µg/L. 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 V, Fe and ^{65}Cu (^{63}Cu does not suffer from interferences in this relatively simple matrix), all of which were acquired in helium mode.

Figures 1 to 3 display the calibration profiles for selected interfered elements with and without cell gas applied; Figures 4 and 5 illustrate the calibration profiles for Be (low mass, difficult to ionize) and Hg (high mass, difficult to ionize, low-abundance isotope). The line does not pass through the origin in the calibrations for those elements that suffer from an interference and this offset can be seen clearly. Be and Hg are also presented to demonstrate the excellent sensitivity for these difficult-to-ionize elements. In order to obtain low detection limits, it is essential to maximize the ion-

ization 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) and plasma generator design (27.12 MHz, solid-state fixed frequency, and high-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 low-mass ion transmission efficiency, further improving the DL of this important and relatively difficult element.

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

Table 3 displays the quantitative data for all samples, including a spike recovery for the Islay whisky. Data are displayed in the preferred cell gas mode (usually helium). Although some elements were calibrated under gas and no-gas conditions, only the most appropriate cell mode is displayed to simplify the data set. Taking Cr as an example, the data for both isotopes did not match in no-gas mode and were significantly higher than the data obtained in helium mode due to the intensity of the C- and Cl-based interferences. The helium mode data for both Cr isotopes produced comparable results, which is a good indication of the accuracy of the data.

The two samples that had been stored in lead crystal decanters have obviously higher Pb concentration in comparison to the other samples. The mean Pb concentration in the noncrystal samples was about 1.3 µg/L, while the Pb content of the samples stored in the crystal decanters was almost 10x higher. As a comparison, the UK maximum permissible Pb concentration in drinking water is 25 µg/L (at the tap), which means that the Pb concentration is within this guideline; however, in 2013 this level is due to be reduced to 10 µg/L, meaning products stored in crystal would fail to meet drinking water quality standards.

Table 2. Limit of Detection, Background Equivalent Concentrations, and Regression Coefficients for the Studied Isotopes (Data are presented as ng/L [ppt] and are corrected for dilution.)

Element	Mass	Mode	r	DL	BEC
Be	**9**	**No gas**	**1**	**0.5**	**0.3**
V	**51**	**He**	**1**	**26.8**	**12.2**
V	51	No gas	0.9999	495	5220
Cr	**52**	**He**	**1**	**50.4**	**73.7**
Cr	52	No gas	0.985	48600	526000
Cr	**53**	**He**	**1**	**38.6**	**71.3**
Cr	53	No gas	0.9997	2020	52100
Mn	**55**	**He**	**1**	**7.8**	**20.8**
Mn	55	No gas	1	17.5	30.4
Fe	**56**	**He**	**0.9999**	**17.8**	**406**
Fe	56	No gas	1	1160	58300
Co	**59**	**He**	**1**	**0.5**	**3.7**
Co	59	No gas	1	5.6	6.7
Ni	**60**	**He**	**1**	**13**	**38.7**
Ni	60	No gas	1	15.2	73.6
Cu	**63**	**He**	**1**	**10.4**	**41.5**
Cu	63	No gas	1	16.6	59.6
Cu	**65**	**He**	**1**	**18.1**	**36.9**
Cu	65	No gas	1	58.6	230
Zn	**66**	**He**	**1**	**33.9**	**119**
Zn	66	No gas	1	22	171
As	**75**	**He**	**1**	**2.0**	**3.8**
As	75	No gas	1	46.1	382
Se	**78**	**H_2**	**1**	**3.6**	**13**
Se	78	No gas	1	135	1390
Cd	**111**	**He**	**1**	**5.7**	**5.3**
Cd	111	No gas	1	3.3	6.1
Sn	**118**	**No gas**	**1**	**7.8**	**50.5**
Sb	**121**	**No gas**	**1**	**7.1**	**30.8**
Ba	**137**	**No gas**	**1**	**2.8**	**5.3**
Hg	**201**	**No gas**	**1**	**1.7**	**10.7**
Pb	**208**	**No gas**	**1**	**2.1**	**10.2**
U	**238**	**No gas**	**1**	**0.1**	**0.2**

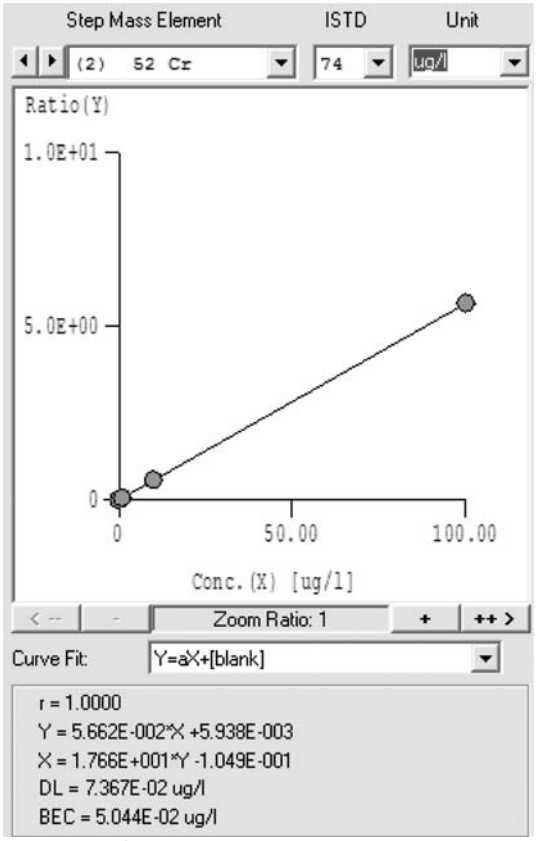

Figure1A. Chromium calibration [He mode]. Note BEC of 0.0504 µg/L.

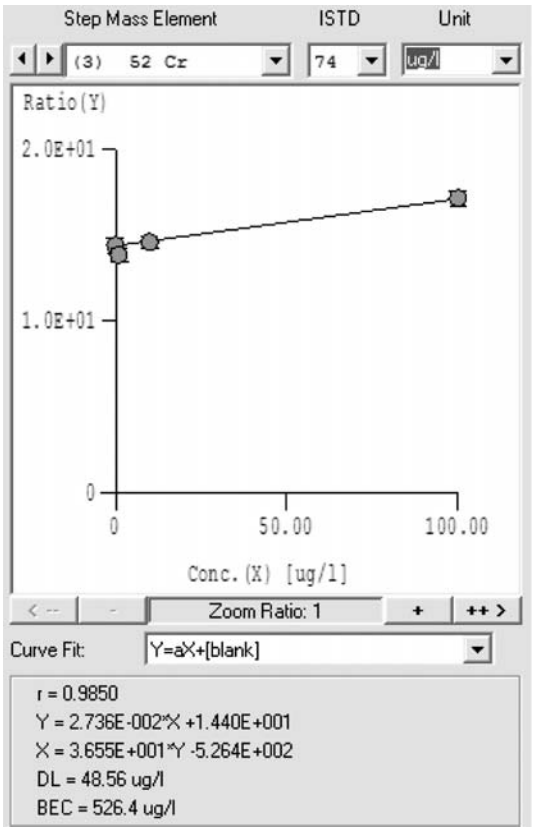

Figure 1B. Chromium calibration [no-gas mode]. Note BEC of 526 µg/L.

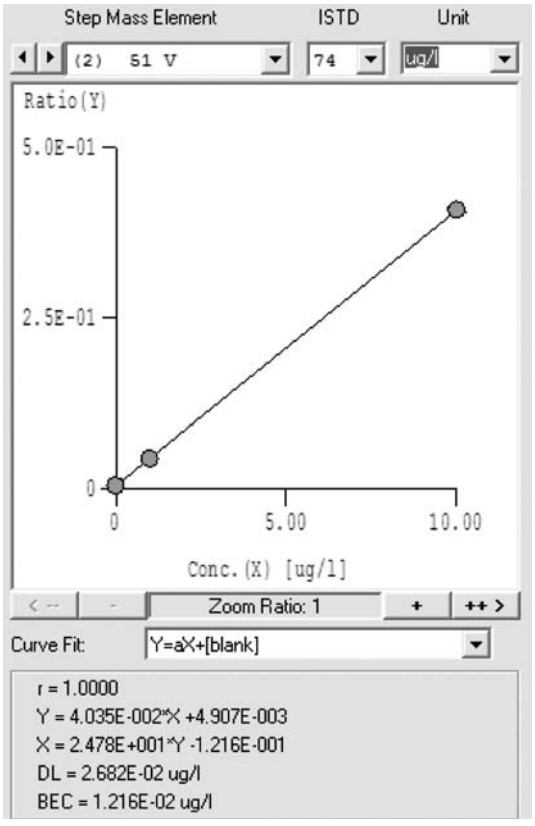

Figure 2A. Vanadium calibration [He mode]. Note BEC of 0.0122 µg/L.

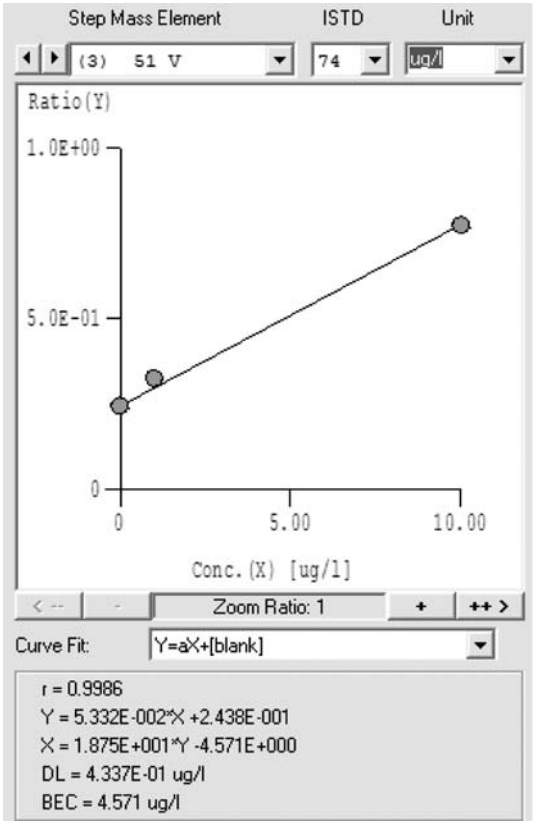

Figure 2B. Vanadium calibration [no-gas mode]. Note BEC of 4.57 µg/L.

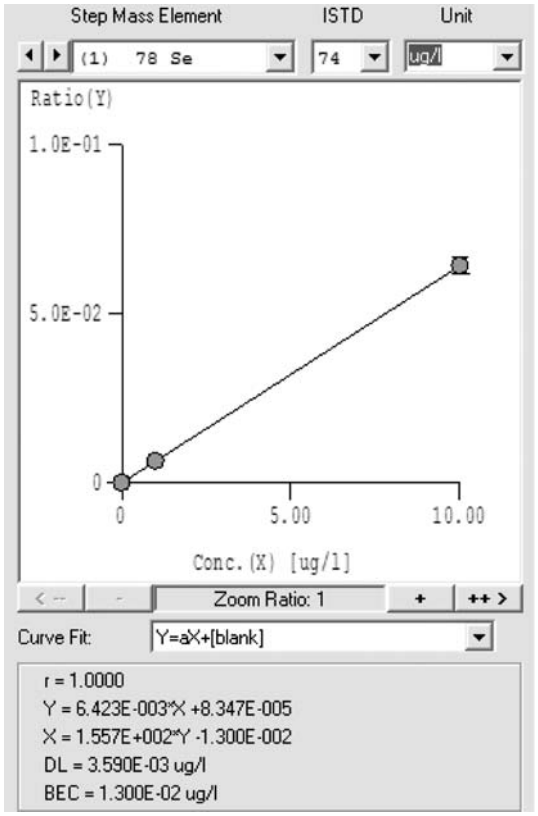

Figure 3A. Selenium calibration [H_2 mode]. Note BEC of 0.013 µg/L.

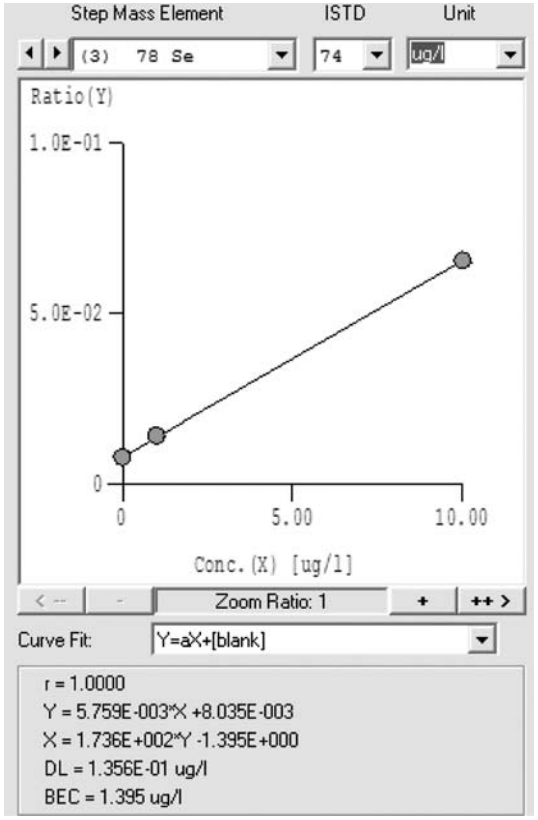

Figure 3B. Selenium calibration [no-gas mode]. Note BEC of 1.4 µg/L.

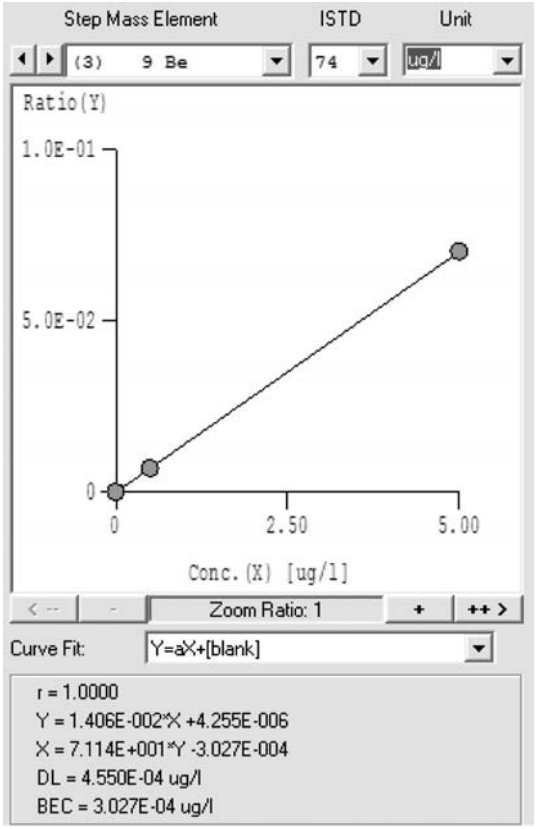

Figure 4. Beryllium calibration [no-gas mode]. Note detection limit of 0.303 µg/L.

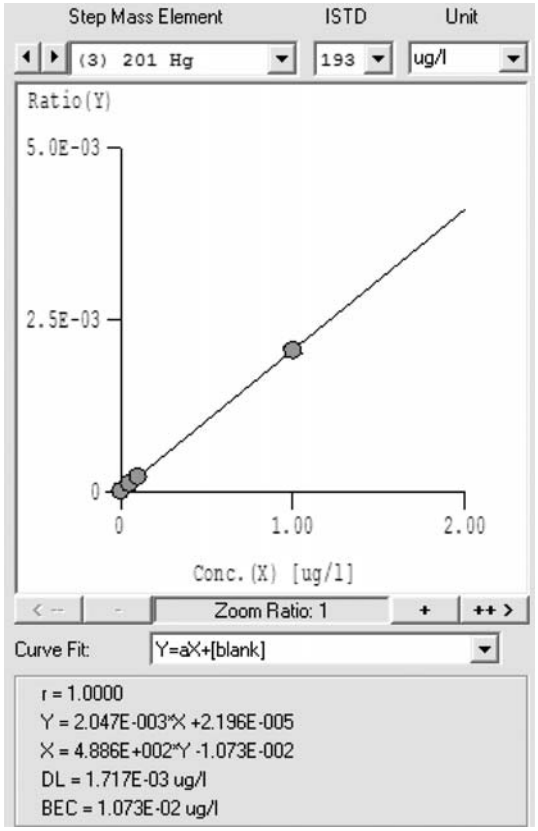

Figure 5. Mercury calibration [no-gas mode]. Note detection limit of 0.0107 µg/L.

Table 3. Quantitative Data Obtained in the Preferred Cell Mode for the Spirit Samples with Spike Recovery for the Islay Sample (Recoveries were generally excellent. All results presented as dilution-corrected µg/L.)

Sample			Highland	Speyside	Islay	Blend	Irish	Bourbon	Bourbon decanter	Whisky decanter	Islay spike	Spike qty	% recovery
Be	9	No gas	0.140	0.052	0.037	0.008	0.035	0.015	0.042	0.048	13.09	12.5	104.4
V	51	He	1.564	0.443	0.344	0.073	0.431	6.321	1.693	0.14	25	25	98.6
Cr	52	He	27.39	14.05	4.064	12.62	22.71	4.077	31.87	4.331	30.95	25	107.5
Cr	53	He	26.15	13.7	3.955	12.57	22.61	3.661	31.52	4.114	30.81	25	107.4
Mn	55	He	54.51	31.76	13.52	12.22	26.95	9.753	90.4	30.54	38.19	25	98.7
Fe	56	He	1125	191.2	99.76	583.8	250.5	131.4	1114	67.03	232.2	125	106.0
Co	59	He	1.097	0.376	0.180	0.130	0.336	0.172	0.323	0.368	12.83	12.5	101.2
Ni	60	He	14.02	3.586	1.442	5.065	3.078	2.274	12.88	1.992	25.91	25	97.9
Cu	63	He	542.9	370.8	454.4	258	38.45	22.2	445.5	367.6	579.8	125	100.3
Cu	65	He	525.5	359.2	441.6	251.4	37.4	21.43	430.8	355.9	568.6	125	101.6
Zn	66	He	21.02	18.54	8.414	14.18	8.149	13.69	68.27	21.9	137.5	125	103.3
As	75	He	0.503	0.427	0.272	0.256	0.164	2.192	0.434	0.424	25.72	25	101.8
Se	78	H_2	0.458	0.357	0.190	0.073	0.045	0.497	0.069	0.293	26.54	25	105.4
Cd	111	He	0.036	0.024	0.012	0.010	0.024	0.036	0.193	0.028	12.55	12.5	100.3
Sn	118	No gas	9.18	14.82	16.68	5.161	2.245	1.681	0.239	15.12	41.3	25	98.5
Sb	121	No gas	0.817	0.514	0.397	0.308	0.311	0.765	0.316	0.188	24.87	25	97.9
Ba	137	No gas	3.282	3.05	1.426	2.001	3.37	3.303	1.396	2.41	25.71	25	97.1
Hg	201	No gas	0.013	0.011	0.010	0.011	0.010	0.018	0.008	0.009	0.252	0.25	97.0
Pb	208	No gas	1.13	0.898	0.903	1.902	1.21	0.912	12.59	11.15	25.33	25	97.7
U	238	No gas	0.295	0.049	0.051	0.026	0.060	0.104	0.028	0.049	24.38	25	97.3

The benefit of operating the instrument in helium mode can clearly be observed for those isotopes suffering from interferences. As helium is a totally inert gas, no side reactions or new product interferences are formed – this lends itself to full mass acquisition allowing interference-free qualitative or semiquantitative analysis. The samples were prepared in an identical way as above (although a separate preparation on a different day) and Table 4 displays the semiquantitative data obtained for the samples analyzed under identical helium cell conditions as with the previous data set.

The full mass spectrum (Figure 6) is from the crystal-stored bourbon sample. The graphic includes an inset, zoomed-in region to demonstrate the excellent isotopic fit for those elements suffering most from interferences. The fit for Cr is particularly important as all three isotopes (50, 52, and 53) demonstrate good agreement with the expected natural ratio in this carbon-based matrix (^{50}Cr suffers interferences from $^{38}Ar^{12}C$, $^{13}C^{37}Cl$, $^{36}Ar^{14}N$, and $^{35}Cl^{15}N$; ^{52}Cr has interferences from $^{36}Ar^{16}O$, $^{40}Ar^{12}C$, $^{35}Cl^{17}O$, and $^{37}Cl^{15}N$; ^{53}Cr has interferences from $^{40}Ar^{13}C$, $^{37}Cl^{16}O$, $^{35}Cl^{18}O$, and $^{35}Cl^{17}O^{1}H$). Several other interferences are also possible, but each is polyatomic in nature and so is removed by the same process and using a single set of helium mode conditions.

To demonstrate instrument stability (Figure 7), 54 separate measurements were made of a spiked Highland malt whisky sample; total measurement time was 5 hours 18 minutes. Stability for the majority of elements was < 2% RSD over the run, indicating applicability of the method to routine analysis.

Table 4. Semiquantitative Data for Spirit Samples Using Helium Mode (Data are presented as µg/L [ppb] unless indicated and are corrected for dilution.)

		Highland	Speyside	Islay	Blend	Irish	Bourbon	Bourbon decanter	Whisky decanter
7	Li	0.24	0.2	0.049	0.084	0.16	0.16	0.34	0.26
9	Be	0.15	N/D	N/D	N/D	N/D	N/D	N/D	N/D
11	B	46	44	42	49	62	69	75	51
12	C	53000 ppm	55000 ppm	55000 ppm	55000 ppm	54000 ppm	76000 ppm	55000 ppm	57000 ppm
23	Na	1400	2100	1600	1600	1000	12000	540	2100
24	Mg	61	48	23	30	63	120	45	48
27	Al	3.9	1.8	1.8	2.3	2.4	1.9	2.5	1.6
29	Si	1300	1400	1300	1300	1300	2000	1500	1400
31	P	13	9.7	6.2	11	86	200	33	18
34	S	100	190	120	240	250	520	210	250
35	Cl	450 ppm	440 ppm	420 ppm	420 ppm	420 ppm	430 ppm	410 ppm	430 ppm
39	K	150	150	100	130	320	470	460	160
43	Ca	60	49	5.5	10	37	18	26	22
47	Ti	0.51	1.6	0.77	0.51	1.5	1.7	0.99	0.8
51	V	0.8	0.54	0.11	0.6	0.6	6.5	1.2	0.21
52	Cr	26	14	5.1	13	23	5.1	27	5.4
55	Mn	54	32	13	14	27	11	90	32
56	Fe	1200	210	100	630	260	150	1100	76
59	Co	1.1	0.47	0.16	0.18	0.36	0.24	0.4	0.4
60	Ni	13	3.5	1.8	5.7	3.4	2.4	13	2.3
63	Cu	530	380	450	260	39	22	440	380
66	Zn	22	18	9	15	8.9	14	71	25
69	Ga	0.65	0.45	0.27	0.39	0.66	0.52	0.3	0.51
75	As	0.44	0.3	0.21	0.2	0.19	2	0.4	0.42
78	Se	N/D	0.48	N/D	N/D	N/D	N/D	N/D	0.47
79	Br	160	150	140	130	120	150	150	150
85	Rb	0.9	1.4	0.92	1	2.2	8.1	6.1	1.5
88	Sr	1.3	0.84	0.22	0.36	1.4	1.7	0.57	0.78
89	Y	0.046	0.03	0.024	0.0084	0.1	0.034	0.0056	0.035
90	Zr	0.18	0.019	0.12	0.064	0.22	0.093	0.069	0.0097
93	Nb	0.0024	0.0076	0.005	0.0051	0.091	0.014	0.0077	0.005
95	Mo	0.7	0.31	0.37	0.41	0.33	1.5	0.76	0.13
101	Ru	0.01	0.02	N/D	0.021	N/D	N/D	0.01	0.02
105	Pd	0.0072	N/D	N/D	0.0075	N/D	0.025	N/D	N/D
107	Ag	0.017	0.027	0.0034	0.0035	0.014	0.0039	0.021	0.01
111	Cd	N/D	0.047	0.047	0.024	0.024	0.1	0.14	0.071
118	Sn	10	18	20	6	3.7	2.2	0.6	17
121	Sb	0.32	0.3	0.27	0.3	0.39	0.8	0.3	0.21
125	Te	N/D	0.38	0.38	0.19	0.19	N/D	N/D	0.18
127	I	0.46	0.42	0.65	0.41	0.5	0.89	0.45	0.47
133	Cs	0.052	0.15	0.026	0.0092	0.063	0.24	0.045	0.15
137	Ba	4.6	3.2	1.3	2.2	3.8	3.8	1.3	2.4
139	La	0.16	0.07	0.063	0.086	0.28	0.15	0.035	0.087
140	Ce	0.47	0.24	0.17	0.11	0.61	0.24	0.04	0.36
141	Pr	0.042	0.028	0.019	0.02	0.063	0.02	0.0044	0.024
146	Nd	0.21	0.12	0.045	N/D	0.3	0.14	0.022	0.14
147	Sm	0.074	N/D	0.01	0.033	0.098	0.037	0.032	0.032
153	Eu	0.0027	0.0083	0.0055	0.011	0.016	0.0063	0.0056	N/D
157	Gd	0.071	0.04	0.048	0.016	0.11	0.056	0.016	0.024
159	Tb	0.0024	0.005	0.0025	N/D	0.012	0.0029	N/D	0.0037
163	Dy	0.071	0.0096	0.024	0.029	0.083	0.028	0.0049	0.029
165	Ho	0.0045	0.0057	0.0057	0.0011	0.012	0.0013	0.0046	0.0034
166	Er	0.1	0.081	0.081	N/D	0.046	0.0075	0.0032	0.078
169	Tm	0.0059	0.003	0.004	0.001	0.0061	0.0046	0.001	0.001
172	Yb	0.055	0.013	0.0043	0.0089	0.013	0.02	0.0044	0.017
175	Lu	0.0018	0.00096	N/D	N/D	N/D	N/D	0.00097	0.00096
178	Hf	0.0096	0.0032	0.0032	0.0033	0.019	N/D	0.0066	0.0032
181	Ta	0.0038	N/D	0.0019	N/D	0.021	0.0011	0.0019	0.00098
182	W	0.11	0.065	0.11	0.13	0.07	0.31	0.07	0.077
185	Re	0.012	0.0049	0.012	0.0051	0.0025	0.0058	0.0076	N/D
189	Os	0.0049	N/D	0.01	0.0051	0.005	0.011	0.005	0.015
195	Pt	0.021	0.026	0.0044	0.018	0.013	0.0051	0.017	0.017
202	Hg	0.057	0.019	0.029	0.029	0.059	0.022	0.039	0.058
205	Tl	0.1	0.084	00.064	0.04	0.041	0.039	0.038	0.052
208	Pb	1.2	0.95	0.94	2	1.3	0.93	12	10
232	Th	0.02	0.0088	0.012	0.0079	0.009	0.027	0.0056	0.0067
238	U	0.26	0.045	0.044	0.023	0.073	0.094	0.032	0.05

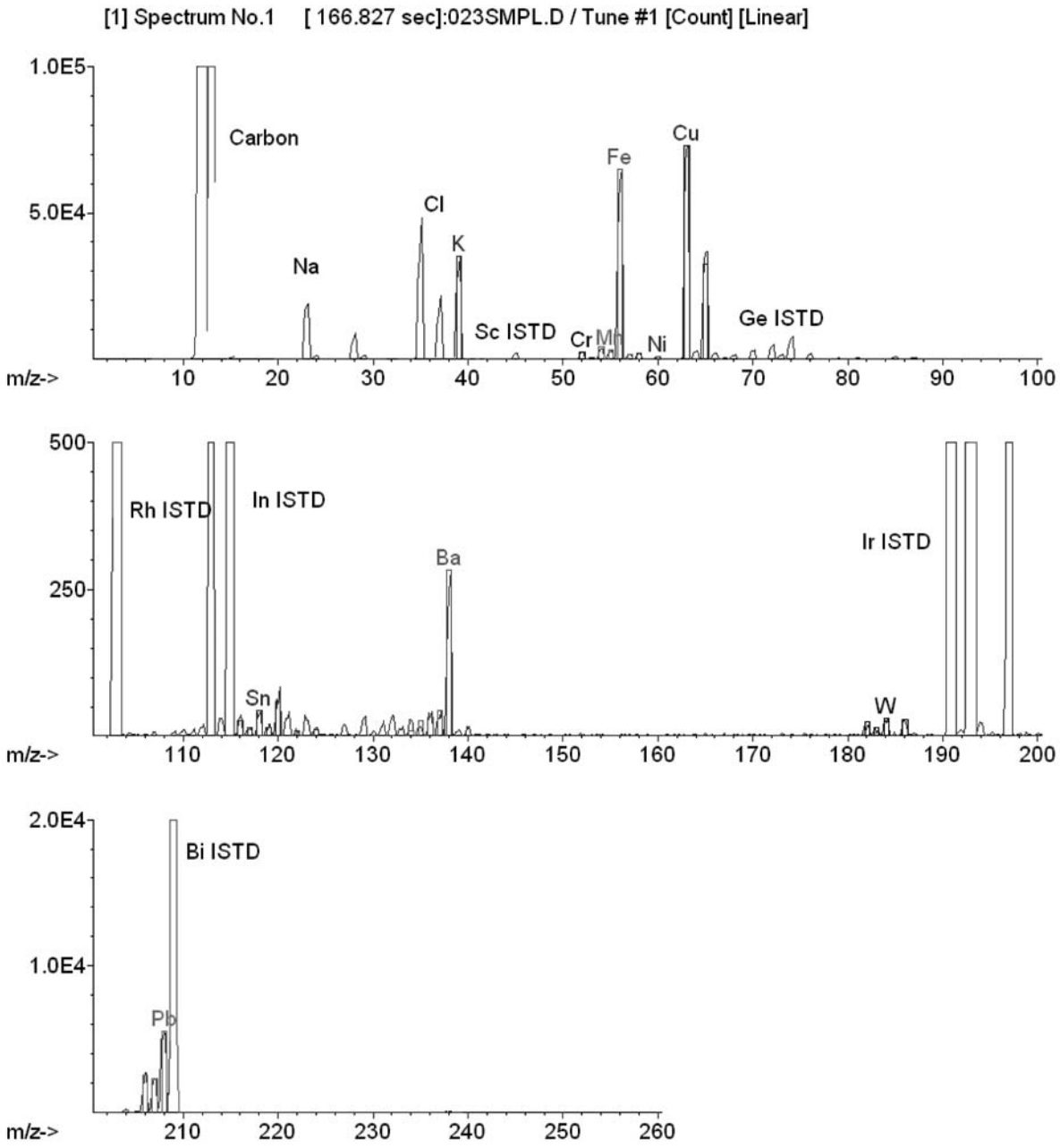

Figure 6a. Full scan (in He mode) of lead-crystal stored bourbon sample. The "major" peaks are indicated, including spectral fit for higher intensity peaks.

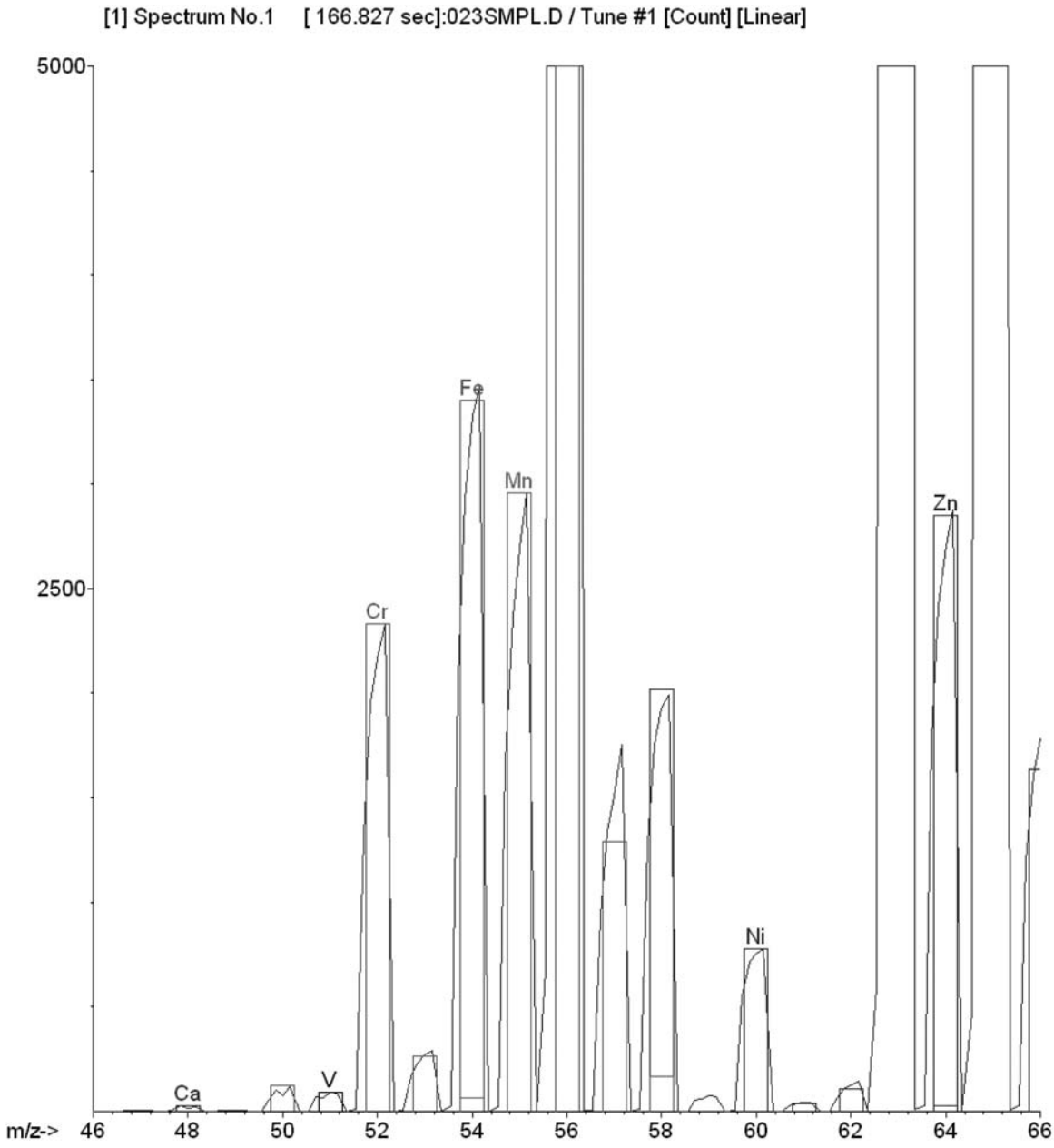

Figure 6b. Zoomed spectrum for those elements suffering from interferences in this matrix. Note good spectral fit, particularly for Cr (suffers from ArO, ArC, and ClO interferences).

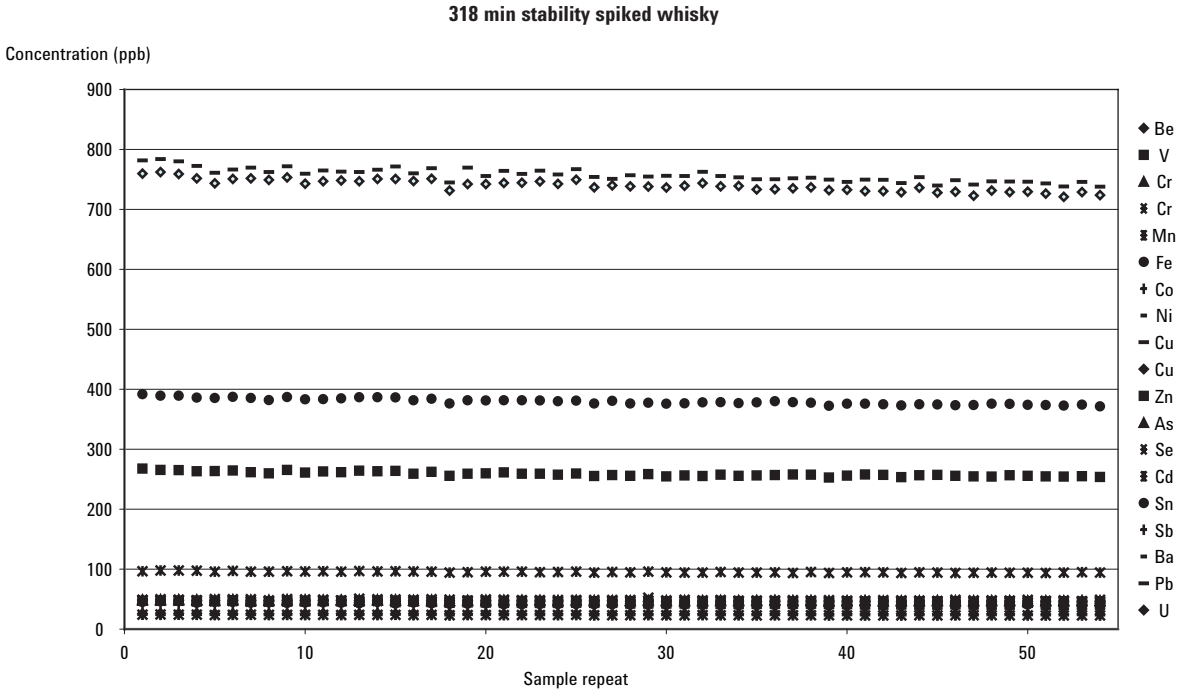

Figure 7. Stability for a spiked Highland malt sample (dilution corrected) taken over 5 hours 18 minutes (54 repeat measurements). Measurement precision was < 2% for almost all elements.

Conclusions

The analysis of high percentage alcoholic beverages using the 7500cx ICP-MS is routine after a simple acidification/dilution. The use of the ORS in the appropriate gas mode efficiently removes the plasma-based and matrix-based interferences, improving detection limits and reliability of the analysis with a simple set of conditions. The use of helium mode also allows interference-free semi-quantitative analysis, permitting greater elemental coverage and rapid screening.

References

1. Achieving Optimum Throughput in ICP-MS Analysis of Environmental Samples with the Agilent 7500ce ICP-MS, Agilent ICP-MS Journal 27, page 4; May 28, 2006, 5989-5132EN

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