Application of the Agilent 7900 ICP-MS with Method Automation function for the routine determination of trace metallic components in food CRMs

Application note

Food safety

Authors

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Introduction

The importance of monitoring the elemental content of foods is already well known and a matter of public concern. Regular reports of food contamination have led to increased safety concerns and pressure on food producers and regulators to ensure that adequate monitoring is performed to ensure that toxic trace elements are not present at levels that may be harmful. The nutritional content of foods is also of interest, with fortification of foodstuffs being proposed as a means of improving diet in regions where dietary intake of certain essential elements may be insufficient. A further requirement for food analysis is the detection of fraud related to mislabeling of a food's origin, especially where the value of the foodstuff is strongly dependent on its origin. A relatively new approach for identifying

food origin uses the pattern of trace elements, which in many cases are characteristic of the soil composition in the region of production. Typical examples where trace elements can be useful to identify provenance include wine, beef, rice, olive oil and fruit juice. It has been reported that green onions from Japan could be distinguished from those from China by using concentration data of 11 elements Na, P, K, Ca, Co, Cu, Sr, Cd, Ce, Cs and Tl [1]. In Europe too, determination of 18 elements was reported to provide data that allowed identification of the origin of olive oils [2].

Along with increased public awareness of the role of metals and other elements in foods, governments and regulators are also introducing a higher level of food testing, a process that is increasingly urgent due to the globalization of food supply. The Codex Alimentarius Commission that was established by the Food and Agriculture Organization of the United Nations (FAO) and World Trade Organization (WTO) has been developing international food standards, guidelines and codes of practice for food production and testing, which include maximum concentrations for trace elements Pb, Cd, As, Sn and other metals. For example, the upper limit of Pb concentration in fish is 0.3 mg/kg, and the concentration of Cd must be lower than 0.4 mg/kg in brown rice, 0.2 mg/kg in wheat and 0.1 mg/kg in potato.

Together with the increased testing requirement, the trend is for a wider range of elements to be monitored, and the regulated levels typically decrease as toxicity becomes better understood. As a result, a fast, multi-element analysis technique with high sample throughput and low limits of detection is preferred for routine food analysis, which means that many food laboratories are now considering or already using ICP-MS for these measurements.

Although an experienced ICP-MS laboratory would typically be able to implement a new food analysis method fairly easily, the adoption of new analytical instrumentation can be challenging for food testing laboratories that have previously used techniques such as ICP-OES and AAS. Trace level analysis requires tighter control of general laboratory practice to ensure that the low detection limits can be achieved routinely. ICP-MS is also generally considered more difficult to use than the well-established ICP-OES and AAS techniques, with one perceived drawback being the greater complexity of developing a reliable analytical method for new sample types. Selection of suitable analyte isotopes and internal standard elements requires some experience, while identifying and dealing with potential interferences requires an understanding of mass spectrometry. The introduction of collision reaction cell (CRC) technology for ICP-MS makes it possible to eliminate most common polyatomic interferences that occur in the sample types typically encountered in a food laboratory, but choosing the optimum cell gas conditions for trace levels analysis in foods also requires some expertise. The Agilent 7900 ICP-MS uses ICP-MS MassHunter software, and the most recent revision includes a new Method Automation function, which simplifies the process of method development, making it easier for users of all levels of experience to develop reliable methods for their particular sample types. This report describes the use of the Agilent 7900 ICP-MS, running a method developed using the Method Automation function, for trace elemental analysis of fish certified reference materials (CRMs).

Experimental

Instrumentation and reagents

An Agilent 7900 ICP-MS with Ultra High Matrix Introduction (UHMI) option and H_2 cell gas option was used for all measurements. In this application, having UHMI available allowed Method Automation to select from a greater range of plasma modes, so a wider range of sample matrix levels can be addressed within the automated method setup. Similarly, as the 7900 ICP-MS had the H_2 cell gas line fitted, Method Automation was able to select H_2 mode where it gave improved DLs. It should be noted however that He mode provides data that easily reaches the regulated limits for all elements routinely monitored in food analysis. The standard sample introduction system was used throughout, consisting of a glass concentric nebulizer, quartz spray

chamber and quartz torch with 2.5 mm internal diameter injector. The standard Ni-tipped interface cones were used. An Agilent ASX-520 autosampler was used to deliver the samples, which were held in 50 mL vials. For digestion of food CRMs, a Milestone ETHOS 1 Advanced Microwave Digestion System was used. 0.5 g of sample was weighed accurately and placed in a digestion tube, and then 7 mL of HNO_3 and 1 mL of HCl were added to the tube. After 20 minutes room temperature digestion, microwave heating was applied, using the heating program shown in Table 1. It is well known that carbon present in the sample solution enhances the ICP-MS signal of some elements, notably As, Se and P, although the precise mechanism of the enhancement is unknown [3, 4]. If volatile elements are not required analytes, the carbon can be removed from the food samples by heating during open acid digestion. However, Hg and other volatile elements are typically required analytes in food monitoring, so closed-vessel microwave digestion is the typical standard method of sample digestion for ICP-MS. With the high digestion temperature used in this work (210 °C), the carbon matrix would have been effectively decomposed during digestion. The effect of any residual carbon in the samples can be mitigated by ensuring that there is an excess of carbon in all samples, for example by adding 2% butan-1-ol online with the internal standard solution.

Table 1. Microwave heating program

Step	Power (W)	Temp (°C)	Time (min)	Mode
1	1000	50	2	Ramp
2	0	50	3	Hold
3	1000	120	7	Ramp
4	1000	120	2	Hold
5	1000	210	15	Ramp
6	1000	210	15	Hold
Ventilation			40	
Cooling with water			60	

The CRMs used for this study were DORM-4 (fish protein) from NRC-CNRC, CRM 7402-a (cod fish tissue) and CRM 7403-a (swordfish tissue) from National Metrology Institute of Japan (NMIJ). High purity reagents 68% HNO_3 and 36% HCl (Ultrapur-100 grade) were purchased from Kanto Chemicals, Japan. The calibration solution was prepared from Agilent Mixed Stock Standard (4183-4682) with Hg and Sn added from single element standards (SPEX Certiprep).

Method building

The Method Automation function or "Method Wizard" function of ICP-MS MassHunter 4.1 can operate in either manual or, for the 7900 ICP-MS, fully automatic mode. In manual mode, available for all supported Agilent ICP-MS mainframes, the user is prompted to enter some information about total dissolved solids concentration of their samples and select analyte elements. The Method Wizard then optimizes the acquisition for either fastest sample throughput or lowest possible detection limits. This mode is suitable for familiar sample types, when the operator has some expertise in ICP-MS and is mainly interested in simplifying the task of method development.

In automatic mode, the Method Wizard automatically selects the most appropriate operating conditions (plasma mode and tuning conditions), analyte isotopes, integration times, cell gas modes and internal standards, based on the current instrument configuration and the composition of the user's own reference sample, which is measured as part of the method setup. The workflow for developing a new method is:

1. The operator is requested to input the desired analyte elements.

2. The operator is prompted to select the autosampler vial positions for:
    a. The blank solution (2% HNO_3)
    b. The Agilent tuning solution (for optimization)
    c. The reference stock standard solution (for calibration)
    d. A sample solution that is representative of the sample type to be measured.
3. The operator is then requested to choose "Rapid Analysis (Speed)" mode or "Lower Detection Limit (Low DL)" mode.

Once this information has been entered, the method building starts automatically. The workflow is illustrated in the screenshots presented in Figures 1 to 3.

From the measurement of the tuning solution, the sample uptake and rinse times are calculated. The total dissolved solids (TDS) level and major element composition are derived from the results of the semi-quantitative analysis of the typical sample. The measured TDS level is used to determine the appropriate plasma mode (Low Matrix, General Purpose, UHMI-4, -8, -25), and the major element composition is used to identify potential matrix-based interferences and select the most appropriate cell mode (no gas, He, High Energy (HE)He, H_2), isotope, integration time and ISTD for each analyte.

In the case of these samples, the preliminary measurement of the representative sample was performed automatically using UHMI-25 and He cell mode, i.e., conditions appropriate for samples with unknown dissolved solids level and matrix composition. For the sample analysis, "Low Matrix" plasma mode was selected by Method Automation, based on the total matrix level assessed during the screening acquisition.

Results and discussion

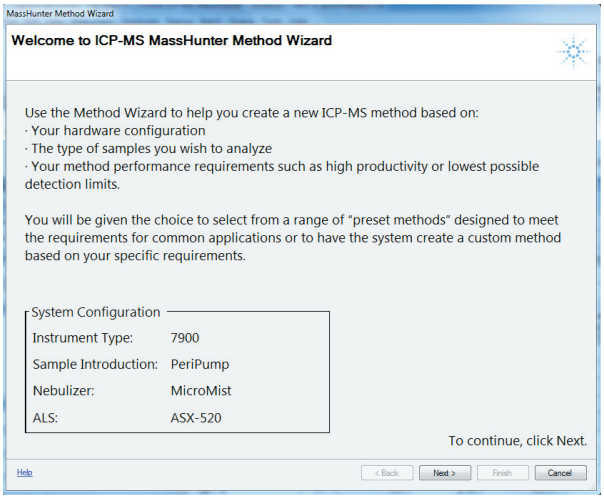
DORM-4 CRM was used as the "typical sample matrix" required by the Method Wizard to optimize the analysis parameters. The plasma and ion lens parameters selected by the Method Automation software are shown in Table 2. The plasma mode is selected based on the total dissolved solids (TDS) concentration of the typical sample measured during the method setup and, since in this case the digestion resulted in a TDS level of below 1000 ppm, "Low Matrix" mode was selected by the Method Wizard. The method parameters selected by the Method Wizard are shown in Table 3 for the sample uptake time and rinse times, and Table 4 for the acquisition parameters. Ion optic settings were also automatically optimized for each ORS mode.

Table 2. Parameters set by the Method Automation software

Parameter	Value			
Plasma mode	Low matrix			
ORS mode	No gas	H_2	He	HEHe
RF power	1550 W			
Sampling depth	8 mm			
Carrier gas	1.05 L/min			
Ext 1 lens	0 V			
Ext 2 lens	-140 V			
He flow rate			4.3 mL/min	10 mL/min
H_2 flow rate		6 mL/min		

Table 3. Sample uptake and rinse time

	Time	Peri-pump speed
Sample uptake	44 sec	0.3 rps
Stabilize	40 sec	0.1 rps
Probe rinse (sample)	10 sec	0.3 rps
Probe rinse (Std)	10 sec	0.3 rps
Rinse 1	40 sec	0.3 rps



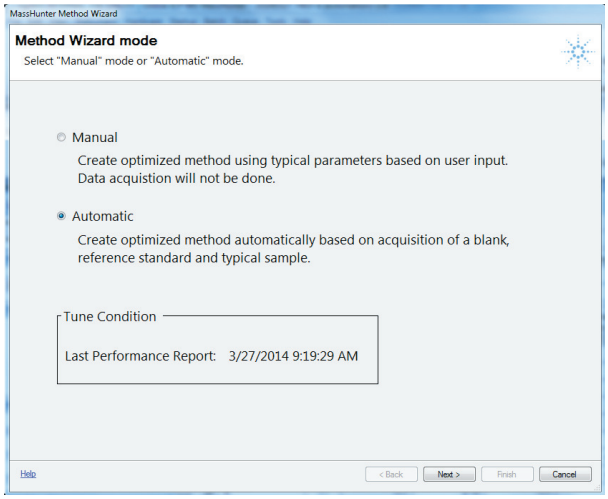
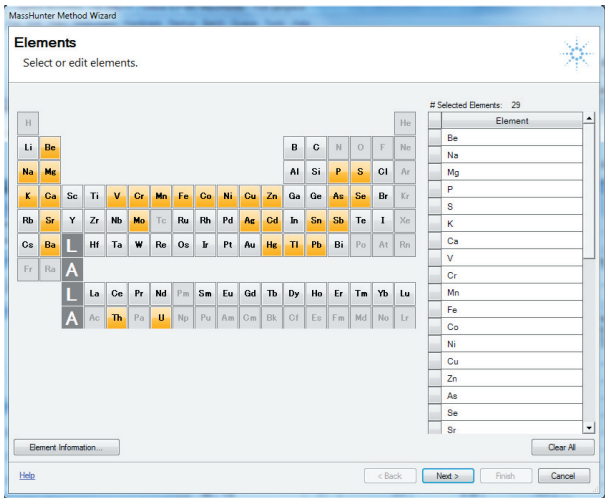


Figure 1. Method summary and hardware configuration are displayed, and the operator selects Method Wizard mode



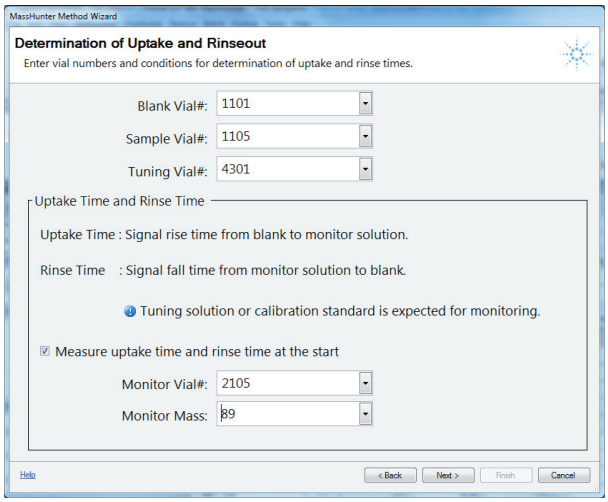
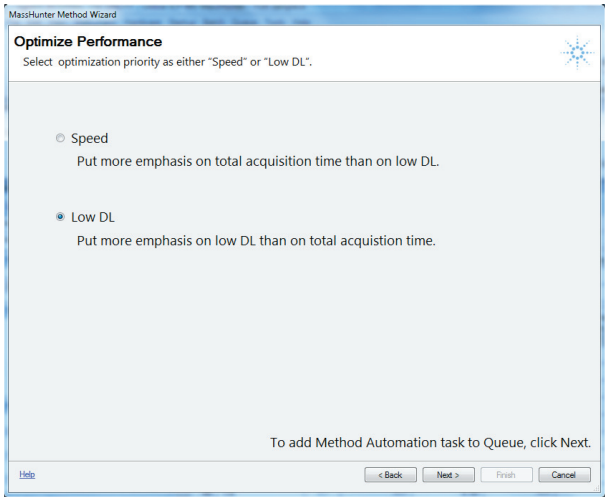


Figure 2. Operator selects analyte elements and vial positions for required solutions, and then chooses predefined ISTD and Calibration stocks



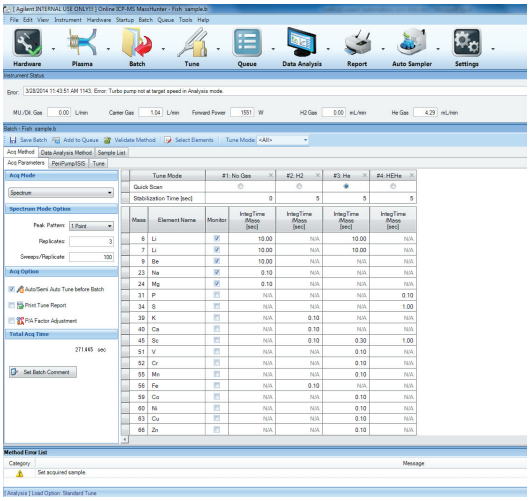


Figure 3. Operator chooses method priority — optimize for highest speed or best detection limits - and method settings are optimized. The optimized method can be used for the new batch acquisition, or saved as a template for future analysis.

Table 4. Analyte parameters selected by Method Automation (Auto-method) compared to comparable parameters selected for this analysis by an experienced ICP-MS chemist (Manual method)

Analyte	Auto-method				Manual method		
	Gas	Mass	ISTD	Integration (sec)	Gas	Mass	ISTD
Be	No gas	9	^{6}Li	10	No gas	9	^{45}Sc
Na	No gas	23	^{6}Li	0.1	No gas, He	23	^{45}Sc
Mg	No gas	24	^{6}Li	0.1	No gas, He	24	^{45}Sc
P	HEHe	31	^{45}Sc	0.1	HEHe	31	^{45}Sc
S	HEHe	34	^{45}Sc	1	HEHe	34	^{45}Sc
K	H_2	39	^{45}Sc	0.1	H_2, HEHe	39	^{72}Ge
Ca	H_2	40	^{45}Sc	0.1	H_2, HEHe	40 (H_2), 44 (HEHe)	^{72}Ge
V	He	51	^{45}Sc	0.1	He	51	^{72}Ge
Cr	He	52	^{45}Sc	0.1	He	52, 53	^{72}Ge
Mn	He	55	^{45}Sc	0.1	He	55	^{72}Ge
Fe	H_2	56	^{72}Ge	0.1	H_2, HEHe	54, 56	^{72}Ge
Co	He	59	^{72}Ge	0.1	He	59	^{72}Ge
Ni	He	60	^{72}Ge	0.1	He	60	^{72}Ge
Cu	He	63	^{72}Ge	0.1	He	63	^{72}Ge
Zn	He	66	^{72}Ge	0.1	He	64,66	^{72}Ge
As	HEHe	75	^{72}Ge	0.1	He, HEHe	75	^{72}Ge
Se	H_2	78	^{72}Ge	0.3	H_2, HEHe	78,82	^{72}Ge
Sr	He	88	^{115}In	0.1	He	88	^{103}Rh
Mo	He	95	^{103}Rh	0.3	He	95	^{103}Rh
Ag	He	107	^{103}Rh	1	He	107	^{103}Rh
Cd	He	111	^{103}Rh	1	He	111	^{115}In
Sn	He	118	^{115}In	1	He	118	^{115}In
Sb	He	121	^{115}In	10	He	121	^{115}In
Ba	He	137	^{115}In	0.1	He	137, 138	^{115}In
Hg	He	202	^{209}Bi	0.3	He	202	^{209}Bi
Tl	He	205	^{209}Bi	1	He	205	^{209}Bi
Pb	He	208	^{209}Bi	0.1	He	208	^{209}Bi
Th	He	232	^{209}Bi	0.1	He	232	^{209}Bi
U	He	238	^{209}Bi	0.3	He	238	^{209}Bi

A range of elements from major to trace levels was determined, focusing on the analytes which have certified reference values in one or more of the 3 CRMs. The results obtained with the 7900 ICP-MS are shown in Table 5, together with the certified values where available. Good agreement with the reference values was obtained in all cases. In order to further validate the method, a spike recovery test was carried out for several elements and the results are shown in Table 6. Excellent spike recoveries were achieved, with most elements being within 95% to 105% recovery.

As a further check to confirm that the method created by the Method Wizard uses conditions that are highly suitable for the analysis being performed, the automatically created method was compared to a method developed independently by an experienced applications chemist. The manually created method settings, which are included in Table 4, use more isotopes and multiple gas modes for some analytes, which expert users often do to allow confirmation of the preferred mode, but the general acquisition settings are almost identical between the two methods.

Conclusions

The method created automatically by the Method Automation function of the ICP-MS MassHunter software was demonstrated to generate accurate data for all certified major and trace elements studied in a range of food certified reference materials. The method settings proved to be almost identical to those chosen independently by a skilled ICP-MS applications chemist. This confirms that the Method Wizard is able to identify the most appropriate isotope and integration time for each analyte, depending on the current instrument configuration and the sample matrix, and assign the best cell mode and internal standard for each analyte. The automatically created method can be applied to major and trace elements, covering the range of analytes typically reported in food samples. The same Method Automation approach can be used for other sample types such as environmental, geological, clinical and pharmaceutical, greatly simplifying method development for routine laboratories in these fields.

Table 5. Analytical results of food CRMs measured using method created by ICP-MS MassHunter's Method Automation function

Analyte	Unit	DORM-4 (fish protein)		7402-a (cod fish tissue)		7403-a (swordfish tissue)	
		Concentration	Certified	Concentration	Certified	Concentration	Certified
9 Be [No gas]	mg/kg	0.01 ± 0.00		N.D. (<0.0008)		N.D. (<0.0008)	
23 Na [No gas]	g/kg	12.9 ± 0.3		3.4 ± 0.1	3.6 ± 0.2	3.57 ± 0.07	3.57 ± 0.12
24 Mg [No gas]	g/kg	0.81 ± 0.01		1.29 ± 0.03	1.34 ± 0.03	1.60 ± 0.03	1.58 ± 0.04
31 P [HEHe]	g/kg	7.6 ± 0.2		10.8 ± 0.1	12	14.5 ± 0.2	14.5 ± 0.4
34 S [HEHe]	g/kg	8.7 ± 0.2		10.4 ± 0.1		8.43 ± 0.06	
39 K [H_2]	g/kg	12.6 ± 0.6		21.3 ± 1.2	22.3 ± 1.0	25.5 ± 0.8	26.3 ± 1.1
40 Ca [H_2]	g/kg	2.18 ± 0.11		0.46 ± 0.03	0.52 ± 0.05	0.196 ± 0.014	0.189 ± 0.009
51 V [He]	mg/kg	1.50 ± 0.01		N.D. (<0.014)		N.D. (<0.014)	
52 Cr [He]	mg/kg	1.75 ± 0.09	1.87 ± 0.16	0.67 ± 0.00	0.72 ± 0.09	0.058 ± 0.001	
55 Mn [He]	mg/kg	3.02 ± 0.11		0.41 ± 0.03	0.41 ± 0.03	0.190 ± 0.004	0.201 ± 0.010
56 Fe [H_2]	mg/kg	339 ± 20	341 ± 27	11.2 ± 0.5	11.2 ± 0.9	13.6 ± 0.7	13.1 ± 0.5
59 Co [He]	mg/kg	10.7 ± 0.09		0.030 ± 0.003	0.04	0.015 ± 0.001	
60 Ni [He]	mg/kg	1.26 ± 0.11	1.36 ± 0.02	0.40 ± 0.10	0.38 ± 0.05	0.076 ± 0.037	
63 Cu [He]	mg/kg	15.8 ± 0.1	15.9 ± 0.9	1.13 ± 0.02	1.25 ± 0.07	1.26 ± 0.02	1.31 ± 0.04
66 Zn [He]	mg/kg	49.3 ± 0.5	52.2 ± 3.2	20.5 ± 0.2	21.3 ± 1.5	33.3 ± 0.2	33.6 ± 1.0
75 As [HEHe]	mg/kg	6.73 ± 0.08	6.80 ± 0.64	36.4 ± 1.1	36.7 ± 1.8	6.77 ± 0.13	6.62 ± 0.21
78 Se [H_2]	mg/kg	3.47 ± 0.12	3.56 ± 0.34	1.8 ± 0.1	1.8 ± 0.2	2.11 ± 0.06	2.14 ± 0.11
88 Sr [He]	mg/kg	9.72 ± 0.10		1.74 ± 0.03	2	1.08 ± 0.02	1.13 ± 0.03
95 Mo [He]	mg/kg	0.261 ± 0.005		0.010 ± 0.006	0.01	N.D. (<0.0008)	
107 Ag [He]	mg/kg	0.022 ± 0.001		N.D. (<0.0050)		N.D. (<0.0050)	
111 Cd [He]	mg/kg	0.304 ± 0.001	0.306 ± 0.015	0.009 ± 0.000	0.009	0.152 ± 0.003	0.159 ± 0.006
118 Sn [He]	mg/kg	0.077 ± 0.004	0.056 ± 0.010	0.016 ± 0.002		0.036 ± 0.001	
121 Sb [He]	mg/kg	0.009 ± 0.000		0.014 ± 0.001	0.02	0.002 ± 0.001	
137 Ba [He]	mg/kg	5.01 ± 0.03		0.027 ± 0.002		2.4 ± 0.02	
202 Hg [He]	mg/kg	0.358 ± 0.004	0.410 ± 0.055	0.53 ± 0.01	0.61 ± 0.02	5.02 ± 0.02	5.34 ± 0.14
205 Tl [He]	mg/kg	0.001 ± 0.002		N.D. (<0.010)		N.D. (<0.010)	
208 Pb [He]	mg/kg	0.405 ± 0.007	0.416 ± 0.053	0.03 ± 0.00	0.04	0.006 ± 0.003	
232 Th [He]	mg/kg	0.177 ± 0.002		N.D. (<0.0008)		N.D. (<0.0008)	
238 U [He]	mg/kg	0.056 ± 0.005		N.D. (<0.0010)		N.D. (<0.0010)	

Table 6. Spike recovery test

	Unit	Spiked	Sample	Found	Recovery %
9 Be [No gas]	µg/L	51	0.071	45.8	88.9
23 Na [No gas]	mg/L	5.1	63.7	68.9	101.3
24 Mg [No gas]	mg/L	5.1	4.0	9.0	97.8
31 P [HEHe]	mg/L	2.5	36.5	38.6	82.8
34 S [HEHe]	mg/L	2.5	42.6	45.1	96.9
39 K [H_2]	mg/L	5.1	N/A*	N/A	N/A
40 Ca [H_2]	mg/L	5.1	11.8	17.1	102.3
51 V [He]	µg/L	51	7.5	55.4	93.2
52 Cr [He]	µg/L	51	8.5	64.2	108.5
55 Mn [He]	µg/L	51	15.8	65.2	96.0
56 Fe [H_2]	mg/L	5.1	1.7	6.8	100.1
59 Co [He]	µg/L	51	1.2	53.0	100.8
60 Ni [He]	µg/L	51	6.3	54.8	94.3
63 Cu [He]	µg/L	51	73.5	122.5	95.3
66 Zn [He]	µg/L	51	242.7	293.3	98.4
75 As [HEHe]	µg/L	51	33.0	84.2	99.7
78 Se [H_2]	µg/L	51	18.2	69.0	98.9
88 Sr [He]	µg/L	514	46.2	591.5	106.1
95 Mo [He]	µg/L	51	1.3	50.4	95.5
107 Ag [He]	µg/L	51	0.1	52.8	102.4
111 Cd [He]	µg/L	51	1.5	52.4	99.0
118 Sn [H_2]	µg/L	0.5	0.4	0.9	96.7
121 Sb [He]	µg/L	51	0.2	47.1	91.3
137 Ba [He]	µg/L	51	25.1	76.9	100.7
202 Hg [He]	µg/L	5.1	1.8	6.9	100.0
205 Tl [He]	µg/L	51	0.1	51.0	99.0
208 Pb [He]	µg/L	51	1.9	53.0	99.3
232 Th [He]	µg/L	51	0.9	52.7	100.8
238 U [He]	µg/L	51	0.3	51.2	99.0

*unspiked sample concentration too high for spike level used.

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Published May 30, 2014
Publication number: 5991-4556EN

Agilent Technologies