Determination of Heavy Metals and Nutrient Elements in Alternative Protein Foods Using ICP-MS

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Introduction

Testing foods using ICP-MS

- To ensure that non-meat based protein and alternative protein products are safe for consumption, manufacturers must comply with Good Manufacturing Practices (GMP).
- GMP guidelines provide guidance for manufacturing, testing, and quality assurance of foods.
- Food safety analysis includes testing for chemicals, e.g., organic contaminants such as pesticide residues, and inorganic contaminants such as heavy metals.
- Labs typically use standard test methods to meet regulations in their jurisdiction.
- A method published in the US Food and Drug Administration Elemental Analysis Manual (EAM) 4.7 was used in this study.
- EAM 4.7 is a comprehensive method for the determination of 12 elements in food digests by ICP-MS.[1]

Insect protein could be a viable and sustainable alternative to meat.

EAM 4.7 method requirements

EAM 4.7 stipulates that an ICP-MS used for FDA regulated food analysis must be able to operate in helium (He) mode with kinetic energy discrimination (KED). Reactive cell gases are not an acceptable alternative on single quadrupole ICP-MS, due to the risk of creating new spectral overlaps through the formation of reaction product ions.

Agilent ICP-MS instruments include advanced features and accessories, which simplify the generation of the high-quality, multi-element data sets needed for food studies:

- Octopole Reaction System (ORS[4]) cell with Shield Torch System for ion energy control: This unique combination provides the most effective control of common polyatomic ion interferences using He collision mode and KED. This saves time by simplifying method setup and provides accurate and precise data, without the need for reaction gases in typical applications.
- Ultra High Matrix Introduction (UHMI) system for direct analysis of 25% total dissolved solids (TDS): UHMI practically eliminates matrix suppression, so results are more consistent for variable, high matrix samples, and labs don't need to waste time preparing matrix-matched calibrations. Provides better matrix decomposition, so less signal drift, fewer QC failures, and less frequent maintenance, another time saving.
- ISIS discrete sampling accessory: High-speed uptake pump, and close-coupled, seven-port switching valve doubles throughput and reduces the amount of sample that reaches the interface.

Experimental

Instrumentation

An Agilent 7850 ICP-MS, which includes the ORS[4] collision cell and UHMI aerosol dilution system, was fitted with the ISIS 3 discrete sampling system (Fig. 1). The ICP-MS was configured with a MicroMist glass concentric nebulizer, and quartz torch with 2.5 mm id injector. The interface consisted of a nickel-plated copper sampling cone and a nickel skimmer cones. Instrument operating conditions are listed in Table 1.

Table 1. Agilent 7850 ICP-MS operating conditions. *Settings for high energy helium (HEHe) mode.

Parameter	Setting
RF Power (W)	1600
Sampling Depth (mm)	10
Carrier Gas Flow (L/min)	0.80
Dilution (UHMI) Gas Flow (L/min)	2.0
Lens Tune	Autotune
Helium Flow Rate (mL/min)	5 (10*)
KED (V)	5 (7*)

Fig. 1. 7850 ICP-MS (top), UHMI (middle), and ISIS (bottom).

Experimental

Sample preparation using microwave digestion as described in EAM 4.7

- Samples were prepared using a MARS 6 closed-vessel microwave digestion system at CEM, USA (Figure 2).
- Approximately 0.5 g of food or SRM was weighed into vessels and 5 mL of HNO_3 and 1 mL of H_2O_2 was added. The heating program is shown in Table 2.
- Finally, 0.5 mL concentrated HCl was added to the digests, followed by de-ionized water to a final weight of 50 g.

Figure 2. MARS 6 microwave digestion system.

Table 2. Heating program.

Parameter	Setting
Power (W)	1800
Temperature (°C)	200
Ramp Time (min)	20
Hold Time (min)	15

Results and Discussion

Verification of instrument calibration and sample digestion process

- To verify the sample digestion process and the accuracy of the analytical method, three certified reference materials (CRMs): NIST 1566b - Oyster Tissue, NRC DOLT-4 -Dogfish Liver, and NRC DORM-4 Fish Protein were analyzed using the 7850 ICP-MS.
- The mean concentrations were in good agreement with the certified concentrations (where available), meeting the QC criteria requirements of the FDA EAM method of 80–120%.

Table 3. CRM results. Units: mg/kg. Blank cells indicate the absence of a certified or reference value.

	1566B Oyster Tissue				DOLT 4 Dogfish Liver				DORM 4 Fish Protein			
Element	Certified Conc	Mean Measured Conc	Recovery (%)	QC Criteria	Certified Conc	Mean Measured Conc	Recovery (%)	QC Criteria	Certified Conc	Mean Measured Conc	Recovery (%)	QC Criteria
^{23}Na	-	3215	-		6800	6743	99	Pass	-	13892	-	
^{24}Mg	-	1107	-		1500	1437	96	Pass	-	887	-	
^{31}P	-	7650	-			12636	-		-	7670	-	
^{39}K	-	6606	-		9800	9499	97	Pass	-	12842	-	
^{43}Ca	838	866	103	Pass	680	769	113	Pass	-	2314	-	
^{52}Cr	-	0.387	-		1.4	1.505	108	Pass	1.87	1.709	91	Pass
^{55}Mn	18.5	19.10	103	Pass	-	10.13	-		-	2.98	-	
^{56}Fe	205.8	208.2	101	Pass	1833	1809	99	Pass	341	325.5	95	Pass
^{60}Ni	1.04	1.09	105	Pass	0.97	1.06	109	Pass	1.36	1.31	97	Pass
^{65}Cu	71.6	72.1	101	Pass	31.2	31.9	102	Pass	15.9	14.85	93	Pass
^{66}Zn	1424	1482	104	Pass	116	122	105	Pass	52.2	49.7	95	Pass
^{75}As	7.65	7.88	103	Pass	9.66	9.31	96	Pass	6.8	6.69	98	Pass
^{78}Se	2.06	2.19	106	Pass	8.3	8.76	106	Pass	3.56	3.70	104	Pass
^{95}Mo	-	0.186	-		1	1.115	111	Pass	-	0.269	-	
^{111}Cd	2.48	2.52	102	Pass	24.3	24.10	99	Pass	0.306	0.293	96	Pass
^{201}Hg	0.0371	0.0406	109	Pass	2.58	2.803	109	Pass	0.41	0.4140	101	Pass
^{205}Tl	-	0.0045	-		-	0.0171	-		-	0.0103	-	
^{208}Pb	0.308	0.3238	105	Pass	0.16	0.1789	112	Pass	0.416	0.4233	102	Pass

Spike recovery and quantitative results

Spike recovery tests were performed to confirm the accuracy of the 7850 ICP-MS method for the analysis of alternative protein food samples. All recoveries were within the acceptable recovery range of the EAM 4.7 method for samples of 80-120% (Table 4). Doubly charged ion interferences on As, Se, and Zn caused by some rare earth elements (REEs) and Ba were avoided using the half mass correction function in the Agilent ICP-MS MassHunter software.

Table 4. Quantitative results and spike recovery data.

			Cricket Protein Powder		Reishi Mushroom Powder		Almond Meal Blanched		Besan (Chick-pea) Flour	
	Conc Units	Spike Level	Native Conc	Recovery Spike (%)	Native Conc	Recovery Spike (%)	Native Conc	Recovery Spike (%)	Native Conc	Recovery Spike (%)
23 Na	mg/kg	17.2	34.4	104	0.197	102	0.0514	100	0.23	101
24 Mg	mg/kg	17.2	11.6	102	4.39	102	28.8	100	10.3	101
31 P	mg/kg	340	91.8	103	10.3	103	55.8	103	24.9	104
39 K	mg/kg	17	101	113	18.6	99	71.9	101	86.1	98
43 Ca	mg/kg	17.4	11.9	103	7.09	100	23.7	101	5.22	102
52 Cr	µg/kg	13.2	1.73	103	155	105	0.582	102	0.613	101
55 Mn	mg/kg	0.066	0.366	113	0.824	100	0.253	100	0.147	99
56 Fe	mg/kg	17.2	0.533	103	2.26	103	0.409	102	0.555	102
60 Ni	µg/kg	13.2	2.14	101	25.9	100	7.16	99	22.1	99
65 Cu	µg/kg	132	291	102	47.1	101	108	100	83.4	99
66 Zn	µg/kg	132	2120	116	72.7	104	297	101	330	104
75 As	µg/kg	13.2	0.364	106	0.865	103	0.232	104	0.0776	104
78 Se	µg/kg	13.2	3.87	103	0.472	102	0.263	105	1.33	103
95 Mo	µg/kg	13.2	7.3	104	0.757	101	4.39	103	6.79	100
111 Cd	µg/kg	13.2	0.118	102	1.38	100	0.121	101	0.00709	101
201 Hg	µg/kg	0.539	0.0287	102	0.522	101	0.0158	102	0.0114	99
205 Tl	µg/kg	13.2	0.0319	102	0.0218	100	0.033	101	0.00867	102
208 Pb	µg/kg	13.2	0.805	105	2.09	102	0.122	102	0.142	102

IntelliQuant data

- In addition to the quantitative analysis, the 7850 can use Quick Scan data to provide IntelliQuant semiquantitative results.
- IntelliQuant determines the approximate concentrations of elements, including elements not included in the calibration standards.
- A heat map of reishi mushroom sample (Figure 3) shows a relatively high concentration of sulfur, plus the presence of strontium and iodine.
- The heat map also shows the presence of REEs in the sample, enabling the automated half mass correction function within ICP-MS MassHunter software to be used.

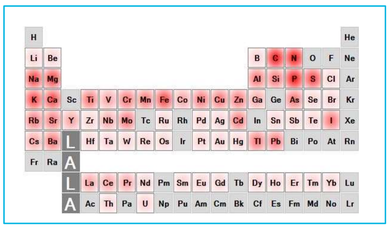

Fig. 3. Periodic table heat map view of ICP-MS IntelliQuant data acquired for the reishi mushroom sample.

Conclusions

Safety, quality, and nutritional testing of insect, fungi, and plant-based proteins using ICP-MS

- Alternative protein samples were accurately measured according to EAM 4.7 method using an Agilent 7850 ICP-MS fitted with an ISIS.
- The risk of doubly-charged ion interferences on As, Se, and Zn, which can be problematic in food samples, were automatically reduced in advance by implementing half-mass correction in the ICP-MS MassHunter software.
- IntelliQuant provided a complete picture of the elements present in the samples, as data can be reported elements not included in the calibration standards.

Reference

1. Patrick J. Gray, William R. Mindak, John Cheng, US FDA Elemental Analysis Manual, 4.7 Inductively Coupled Plasma-Mass Spectrometric Determination of Arsenic, Cadmium, Chromium, Lead, Mercury, and Other Elements in Food Using Microwave Assisted Digestion, Version 1.2 (February 2020)

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