Sample Preparation and ICP-MS Analysis of Trace Metals in Foods

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Abstract

The Food Safety Modernization Act (FSMA), signed into law in 2018, ushered in a host of new requirements in food testing. The US FDA oversees food safety in the United States. The FDA's Elemental Analysis Manual (EAM) provides guidance on trace metals analysis by ICP-OES (Section 4.4) as well as ICP-MS (Section 4.7). Both of these sections specify microwave assisted digestion to prepare the samples for final analysis. In this study, we digested 10 different food samples, of various nutritional composition, along with reference standards, spikes, and blanks all in a single digestion run. This amounted to a total of 40 samples prepared in the same batch. The total digestion time, including cooling, is 60 min, providing any food testing laboratory the highest throughput possible. We will cover sampling, sample size, acid choice, and digestion method for these sample types. In addition we will provide ICP-MS data to verify the validity of this method.

Introduction

High level exposure to certain heavy metals can cause adverse effects on human health including impaired brain and cognitive development in children, cardiovascular disease, diabetes, and cancer, to name a few. Toxic heavy metals such as As, Cd, Pb, and Hg are present in our air, soil, and water and are persistent once released into the environment. These elements can accumulate in plants, and animals that eat these plants, and make their way into our food supply. Because of the adverse health effects of these metals, the FDA imposes strict limits on the amounts that may be present in the foods we eat.

Procedure and Method

Ten foods, that varied greatly in their fat, protein, and carbohydrate macronutrient profile, were obtained from local retailers. Three SRMs were obtained from NIST. **Figure 1** shows the 10 food samples and 3 NIST SRM samples used in this study and **Figure 2** shows their macronutrient plot. Most samples were digested as received, however, the frozen pizza and chicken pot pie required blending in order to obtain a homogenous representative sample prior to digestion. In addition to the SRM samples, 2 samples were fortified at low and high spike levels as proscribed in EAM 4.7. Additionally, blanks and fortified blanks were prepared. All samples were digested in duplicate, for a total of 40 samples in a single batch.

Figure 1. Samples analyzed in study

Procedure and Method cont'd

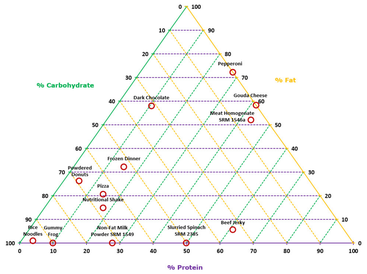

Figure 2. Macronutrient profile of samples and SRMs

All samples were weighed to 0.5 g dry weight equivalent, or 5 mL of liquid, and placed into a 75 mL MARSXpress vessel. Eight mL of concentrated double distilled HNO_3 was added to each vessel and the samples were predigested for 15 minutes. Predigestion allows initial breakdown of the sample, particularly samples high in carbohydrates, at low temperatures and allows for a more controlled digestion upon application of microwave energy. After foaming and gassing subsided, 1 mL of 30% double distilled H_2O_2 was added to each vessel and again, the samples were allowed to predigest for another 15 minutes. After the conclusion of the second predigestion the vessels were sealed and placed into the MARS 6. The Food One Touch Method was selected which heated the samples to 200 °C and held them at that temperature for 15 min.

After the vessels had cooled to 50 °C, the digested samples were transferred to 100 mL vials and diluted to 50 g with DI H_2O. A 0.5 mL aliquot of 12 M HCl was added to stabilize Hg and the samples were further diluted to 100 g with DI H_2O. **Figure 3** shows diluted samples that were clear and particle free.

Samples were then analyzed on an Agilent 7800 ICP-MS using enhanced helium, and high energy helium mode, rather than a reactive gas such as hydrogen or ammonia, to break up higher bond-energy polyatomic ions. Avoiding reactive gasses ensures that no new molecular interferences are formed within the cell, which improves data quality and streamlines the method.

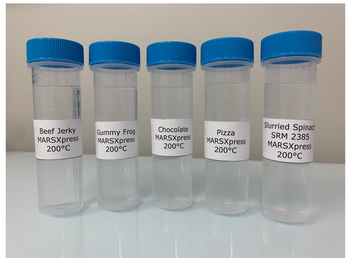

Figure 3. Clear and particle free samples

Results

Table 1 shows results for 6 of the food samples. In addition to the 11 elements specified in EAM 4.7, data for Al, V, Fe, Sb, Ba, Tl, Th, and U was also produced.

Since there was concern about doubly charged interferences, arising mostly from rare earth elements like neodymium (for arsenic) and gadolinium (for selenium), these elements were measured at half mass.

Results

Table 1. Quantitative results for food samples

	Beef Jerky	Nutritional Shake	Gouda Cheese	Gummy Bears	Powdered Donuts	Dark Chocolate
^{27}Al	3700 ± 224	746 ± 10	705 ± 131	1390 ± 300	121000 ± 2900	33600 ± 1600
^{51}V	25.6 ± 5.9	7.1 ± 1.9	<DL	30.8 ± 2.8	33.1 ± 1.7	82.3 ± 8.8
^{52}Cr	107 ± 3	197 ± 2	71.9 ± 3.5	162 ± 4	135 ± 9	1540 ± 36
^{55}Mn	2630 ± 120	6400 ± 56	263 ± 4	31.6 ± 2.4	2500 ± 46	20400 ± 110
^{56}Fe	54200 ± 1400	23900 ± 227	1270 ± 1	1710 ± 27	15600 ± 200	127000 ± 2100
^{59}Co	1.0 ± 0.2	<DL	<DL	<DL	<DL	538 ± 4
^{60}Ni	259 ± 66	57.5 ± 6.4	34.6 ± 2.6	157 ± 5	193 ± 33	5080 ± 35
^{63}Cu	1200 ± 30	2590 ± 22	210 ± 4	<DL	543 ± 25	18700 ± 148
^{66}Zn	82400 ± 1890	21900 ± 189	43900 ± 260	<DL	4380 ± 50	39700 ± 320
^{75}As	13.2 ± 0.4	6.6 ± 0.5	3.4 ± 0.4	7.6 ± 0.6	6.8 ± 0.6	16.3 ± 0.7
^{78}Se*	476 ± 5	131 ± 1	50.6 ± 0.5	<DL	88.9 ± 2.5	98.4 ± 5.7
^{95}Mo	47.7 ± 2.6	227 ± 3	82.5 ± 1.4	9.7 ± 0.6	144 ± 10	218 ± 4
^{111}Cd	31.6 ± 0.7	19.6 ± 0.6	18.9 ± 0.1	18.7 ± 0.1	29.3 ± 0.6	205 ± 2
^{121}Sb	<DL	<DL	<DL	<DL	<DL	<DL
^{137}Ba	577 ± 40	116 ± 3	619 ± 12	77.1 ± 1.3	654 ± 24	7500 ± 28
^{201}Hg	<DL	<DL	<DL	<DL	<DL	<DL
^{205}Tl	<DL	<DL	<DL	<DL	<DL	<DL
^{208}Pb	9.5 ± 0.8	<DL	<DL	<DL	6.7 ± 0.5	29.8 ± 0.9
^{232}Th	<DL	<DL	<DL	<DL	<DL	<DL
^{238}U	<DL	<DL	<DL	<DL	<DL	<DL

Each sample was digested in duplicate and analyzed in triplicate. All six measurements of a single element are within 20% of each other indicating that both the sample preparation and measurement are reliable and repeatable.

Conclusion

Validated food methods generally involve a great deal of quality control. In our EAM 4.7 study, QC internal standard recovery, stability, calibration curve, initial calibration verification, and other relevant quality tests were all within method specifications. Checks on reference material (NIST meat homogenate, nonfat milk, and slurried spinach) concentrations showed agreement with standards of ±20%. Moreover, the fortified method blank was analyzed periodically, throughout the entire method, and found to reside within the method's acceptable range of 90-110%. Values for spike recovery of a fortified analytical portion, and duplicate portions, were also within acceptable ranges.

This data validates the MARS 6 with MARSXpress 75 mL vessels and the Agilent 7850 ICP-MS as suitable instruments for digestion and analysis of compositionally varied food samples.