

## ABSTRACT

Many popular breakfast and bread spreads are natural products composed of fruit, nuts, seeds and yeasts. Children are frequent consumers of many of these popular spreads. Studies of individual spread components such as grapes, nuts and cocoa beans have reported significant amounts of heavy metal contamination. Lead arsenate was the most commonly applied pesticide in fruit & nut orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned. In this study, various samples of bread spreads including fruit spreads, peanut butter, nut butters, yeast spreads and cocoa spreads were tested for heavy metal contamination. Samples were digested using microwave digestion and testing by ICP-MS to determine heavy metal contamination possible in these common foods.

## INTRODUCTION

In countries around the world, nut butter spreads are a staple of the average child's diet. In North America, peanut butter is the most popular bread spread while in Europe, hazelnut spread tops the charts. The largest growth sector for nut butters is Asia as a wide variety of tree nut butters are being introduced into every day diets. In 2018 it is estimated that the nut based and sweet spread products saw €5.75 billion in sales, a 65% increase from 2013.

So, why are nut butters so popular? Nut butters offer a high source of protein and healthy monounsaturated fatty acids as well as a myriad of vitamins and minerals. So how could products which bring so much health benefit be bad for us? Since peanuts and tree nuts are plant based and grown in soil, they are prone to absorb elements contained in the soil. These elements range from uranium, lead, strontium, cadmium, and arsenic from residual fertilizer and pesticide use among other sources of contamination. Many products which are subject to grinding and processing can also become contaminated or adulterated by additives or wear metals from the processing.

This study examined a variety of bread spreads including peanut butter, hazelnut spread, cashew butter, almond butter, sunflower butter, and more to determine concentration of potentially toxic elements which could be of concern.

## MATERIALS

### SPEX CertiPrep Standards

- CLMS-1: ICP-MS Multi-Element Solution
- CLMS-2: ICP-MS Multi-Element Solution
- CLMS-3: ICP-MS Multi-Element Solution
- CLMS-4: ICP-MS Multi-Element Solution
- CL-ICV: Initial Calibration Verification Standard

### Reagents

- High Purity Nitric Acid (HNO<sub>3</sub>)
- DI Water (18 MΩ)

### Samples

- Peanut Butter
- Almond Butter
- Soybean Butter
- Cashew Butter
- Cookie Butter
- Sunflower Butter
- Tahini
- Hazelnut Spread
- Yeast Product Spreads

All samples were purchased from UK, New Jersey and North Carolina supermarkets.

## SAMPLE PREPARATION

### Initial Sample Preparation

Bread spreads were frozen using liquid nitrogen by applying a known amount of sample to a silicone non-stick mold and pouring liquid nitrogen over the sample multiple times in order to flash freeze the sample, see Figure 1. This was done to ensure that all of the sample reached the bottom of the digestion vessel, a task which is difficult when bread spreads are at room temperature.



Figure 1. Sample Preparation of Bread Spreads

### Sample Digestion and Analysis

- Samples digested in CEM MARS 6 iWave Microwave Unit with MARSXpress Plus Vessels (Figure 2)
- 0.25 g of sample added to vessel with 10 mL high purity nitric acid
- The One Touch Method "Food" was used for digestion of all samples and blanks
  - Temperature: 210 °C
  - Ramp: 20 minutes
  - Hold: 15 minutes
  - Power: 220 – 1800 W
- Digestion blanks were run in series with each batch and subtracted from the results that followed them in each series
- Digest of samples were diluted 30 mL then diluted 1:10 before analysis on ICP-MS

Table 1. ICP-MS Elements Monitored

Element	Line	Supplemental Gas
Cr	53	He
As	75	He
Se	77	None
Sr	87	None
Cd	114	None
Sb	121	None
Hg	202	None
Tl	205	None
Pb	208	None
Th	232	None
U	238	None



Figure 2. MARS 6

### Instrument Conditions

Samples run for trace elements on Agilent ICP-MS 7900 using Meinhard nebulizer with cyclonic spray chamber using the lines reported in Table 1. Supplemental helium gas was used to improve the response of Arsenic and Chromium.

## RESULTS

The MARS 6 with MARSXpress vessels was able to completely digest all samples in mixed batches. Figure 3 shows a representative temperature/power curve where the programmed temperature of 210 °C was achieved and held for 15 minutes. The bar graph in the image shows that all vessels reached the same temperature to ensure complete digestion of every sample.

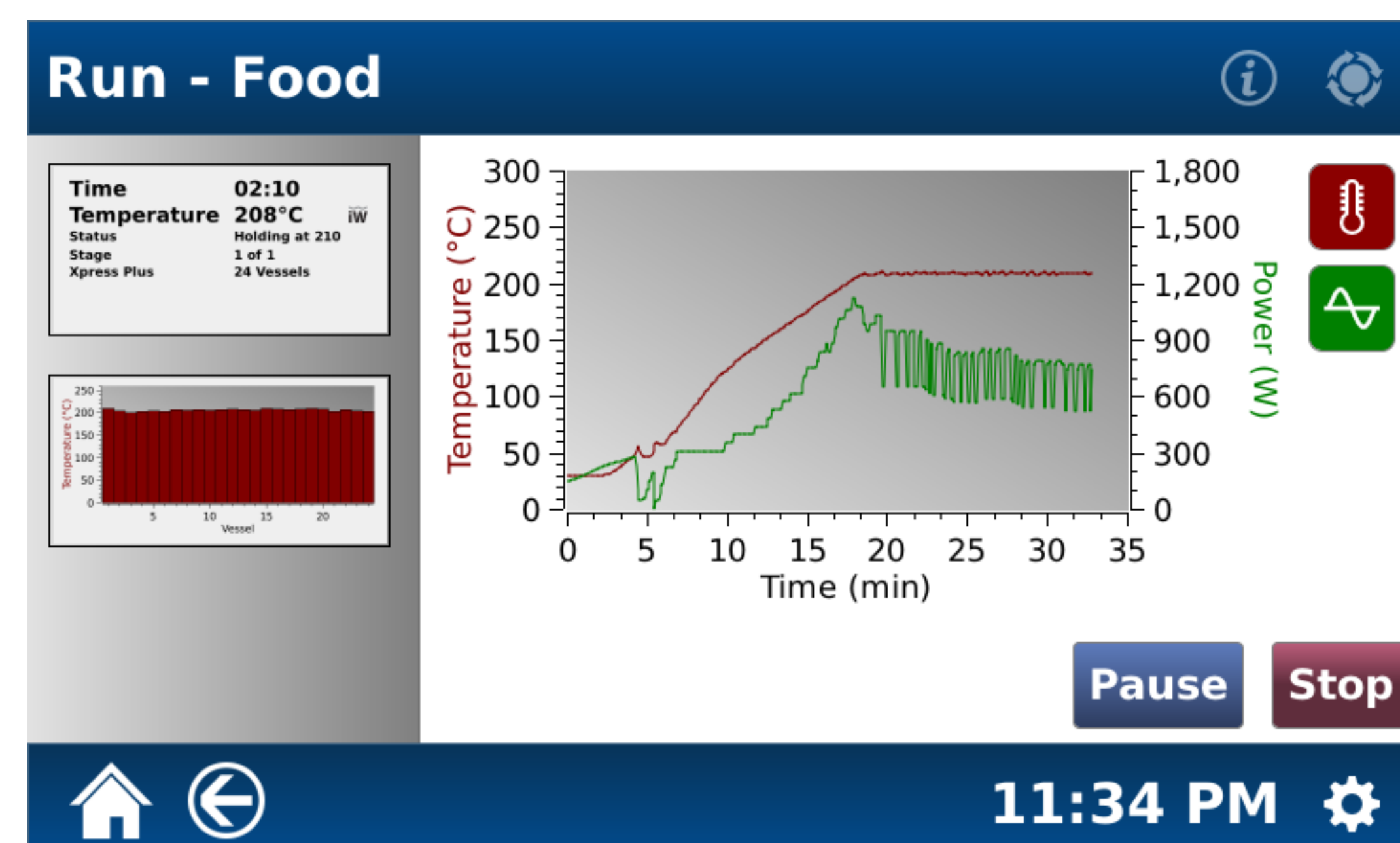


Figure 3. Temperature and Power Graph from Mars 6

ICP-MS analysis results in Table 2 show higher than expected levels of the heavy metals uranium (U), lead (Pb), arsenic (As), strontium (Sr), and cadmium (Cd) in many samples. Interestingly, uranium (U) is present in high levels in tree nut butters including Almond, Cashew, and Hazelnut while very low in peanut butter. This could be due to the length of time the nut spends on the plant prior to harvesting. Also notable was the lead (Pb) levels in some approach maximum daily limits for a child for some regulatory bodies around the world.

Table 2. Heavy Metals Content of Bread Spreads (ug in 30 g [2 tablespoons average serving])

Type	Sample #	Cr	As	Se	Sr	Cd	Sb	Hg	Tl	Pb	Th	U
Almond	57	16.50	2.98	3.84	448.56	1.06	0.91	1.16	0.57	3.59	0.02	9.23
Cashew	60	7.42	3.56	13.29	140.61	0.76	0.99	0.95	0.40	2.97	0.01	8.87
Cashew	64	7.42	2.38	9.28	91.51	0.67	1.01	0.73	0.29	3.15	0.02	8.01
Cookie	63	9.28	3.06	3.83	12.79	0.81	0.81	1.26	0.28	2.60	0.02	7.59
Hazelnut	65	23.46	1.11	2.65	118.46	2.25	0.72	1.56	0.18	1.70	0.05	4.01
Hazelnut	66	16.59	6.44	4.09	127.04	1.03	0.96	1.39	0.36	5.48	0.06	8.79
Hazelnut	67	3.78	2.85	4.15	83.44	0.62	0.92	1.87	0.29	2.89	0.06	7.71
Hazelnut	68	20.55	2.79	2.95	92.15	1.49	0.89	1.54	0.31	4.39	0.05	8.06
Hazelnut	69	21.83	1.45	2.73	58.21	1.08	0.37	0.80	0.13	2.70	0.12	2.87
Multi	48	6.99	0.64	5.34	49.47	2.68	0.20	0.26	0.14	0.62	0.02	1.79
Peanut	28	5.32	0.79	6.08	63.69	1.86	0.16	0.23	0.11	0.74	0.06	1.15
Peanut	29	6.26	0.78	6.42	64.03	1.59	0.18	0.08	0.10	0.90	0.05	1.14
Peanut	30	5.46	0.84	5.47	67.93	1.95	0.23	ND	0.10	0.80	0.07	1.18
Peanut	31	8.98	0.71	8.21	60.41	1.38	0.24	ND	0.08	1.19	0.03	1.04
Peanut	32	5.19	0.56	5.83	71.08	2.63	0.15	ND	0.08	1.00	0.03	1.02
Peanut	33	5.08	0.76	4.60	68.05	2.04	0.19	0.07	0.03	0.92	0.04	0.59
Peanut	34	10.50	0.92	7.80	73.15	1.52	0.11	0.16	0.03	0.95	0.04	0.62
Peanut	34	6.79	1.55	12.07	58.14	0.57	0.69	1.45	0.14	1.74	0.04	3.67
Peanut	35	19.56	0.62	6.66	65.09	1.70	0.21	0.03	0.03	1.52	0.07	0.59
Peanut	36	4.96	0.86	6.10	62.94	1.97	0.20	ND	0.03	0.70	0.03	0.61
Peanut	37	4.98	0.37	6.80	66.32	1.48	0.13	0.03	0.03	0.68	0.01	0.59
Peanut	38	7.30	3.63	7.43	66.17	1.65	0.18	0.15	0.07	1.63	0.07	0.75
Peanut	39	5.41	0.70	7.77	71.17	1.89	0.35	0.07	0.08	0.82	0.04	0.68
Peanut	40	7.02	0.95	8.21	63.68	1.77	0.22	0.22	0.10	1.25	0.05	1.35
Peanut	41	5.58	0.74	6.04	58.13	1.42	0.14	0.13	0.07	1.87	0.06	0.82
Peanut	42	6.02	0.50	10.29	57.93	2.17	0.22	0.20	0.10	1.97	0.04	1.25
Peanut	43	2.03	0.48	6.73	73.70	3.31	0.16	0.22	0.11	0.94	0.03	1.47
Peanut	44	3.15	0.66	7.96	158.10	1.02	0.19	0.14	0.11	1.21	0.03	1.36
Peanut	44	4.38	0.92	34.72	87.16	22.52	0.77	0.58	0.12	1.22	0.01	2.29
Peanut	45	4.78	0.72	11.40	154.10	7.92	0.21	0.28	0.12	0.76	0.02	1.73
Peanut	45	3.59	1.44	10.13	202.81	10.63	0.46	0.81	0.13	1.43	0.02	2.74
Peanut	47	16.04	2.55	29.75	306.70	2.24	0.38	2.44	0.15	1.51	0.03	2.01
Peanut	55	3.61	1.06	14.09	531.38	0.87	0.23	0.29	0.19	0.74	0.01	2.43
Peanut	56	4.20	1.23	7.20	375.25	0.76	0.15	0.26	0.15	0.62	0.07	2.07
Peanut	70	6.67	1.55	48.70	956.35	5.88	0.11	0.52	0.11	0.68	0.03	1.44
Peanut	71	4.99	1.12	7.01	85.35	1.32	0.16	0.25	0.15	1.21	0.04	1.67
Peanut	72	5.24	1.93	1.05	150.37	0.12	0.25	0.15	0.15	1.10	0.04	1.67
Peanut	73	2.75	2.96	1.62	206.55	0.14	0.13	0.01	0.15	0.73	0.06	1.57
Peanut	76	6.32	1.22	13.85	117.91	2.45	0.28	0.32	0.16	4.54	0.10	2.60
Peanut/Date	46	6.80	1.40	8.20	331.39	1.58	0.13	0.19	0.10	0.81	0.19	1.28
Soybean	61	5.08	2.20	13.81	1132.38	0.91	0.55	1.37	0.12	3.41	0.04	4.06
Soybean	62	3.75	1.66	2.91	14.95	0.60	0.49	0.98	0.20	1.50	0.01	3.12
Sunflower	49	6.50	1.77	26.04	79.54	17.66	0.57	1.42	0.15	5.93	0.01	4.09
Sunflower	52	3.73	1.35	4.16	125.66	3.36	0.74	0.69	0.13	1.43	0.03	2.37
Sunflower	53	1.94	0.91	2.97	75.26	7.67	0.61	0.59	0.13	1.31	0.01	2.53
Sunflower	54	4.39	5.25	38.37	205.44	0.52	3.18	0.78	0.60	3.82	0.03	2.12
Tahini	58	5.90	1.15	9.08	417.83	0.87	0.45	0.97	0.15	1.14	0.01	3.11
Tahini	59	18.10	1.16	4.76	408.07	0.35	0.39	0.88	0.10	1.37	0.04	2.78
Yeast	74	5.14	5.41	53.79	123.66	0.60	0.79	0.95	0.14	1.61	0.03	2.59
Yeast	75	4.51	0.66	12.88	156.96	1.13	0.40	0.48	0.11	1.77	0.02	2.19

## CONCLUSION

While peanut and tree nut butters are excellent sources of protein, vitamins, and minerals, one should be aware of the amount of these products that they consume on a daily basis to ensure exposure levels for toxic heavy metals such as lead, arsenic, strontium, and cadmium are minimized. It is also interesting to note that peanut butter seems to contain some of the lowest amounts of toxic metals compared with the tree nut butters.

Manufacturers should be aware of the values of heavy metals contained in their product and should inform consumers of high levels of such metals are present in their products. Heavy metals should be reported as part of the nutritional label to ensure consumer knowledge.